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X-RAYS OF LONG WAVE-LENGTH FROM A RULED GRATING*

By Franklin L. Hunt

Abstract

By the use of a grating ruled on glass (200 lines per millimeter) at grazing incidence (20′ to 40′) in vacuum, the following lines have been obtained: $M\alpha$ of platinum (6A); $K\alpha$ of aluminum (8.3A); $L\alpha$ of copper (13.3A); $L\alpha$ of iron (17.7A); $L\alpha$ of chromium (21.5A); $K\alpha$ of carbon (45.8A). A water-cooled metal x-ray tube with hot lime-coated platinum cathode was used. This was connected directly to the spectrometer with no absorbing film between the anticathode and the photographic plate. Wave-lengths were determined with reference to $L\alpha$ of copper and also directly by calculation from the constants of the spectrometer.

Introduction

IT HAS been shown[1] recently that x-ray spectra can be obtained from a grating ruled on speculum metal if the radiation strike the grating sufficiently near grazing incidence to be within the angle of total reflection.[2] In the experiments referred to the K characteristic radiation of molybdenum and copper were used. It was found necessary first to eliminate the general radiation by reflecting the x-rays from a calcite crystal before they fell on the grating. Further experiments,[3] in which a grating ruled on glass was used, have given some of the strong lines of the K spectrum of copper and iron, thus extending the range investigated directly by this method to approximately 2 Angstrom units. For longer wave-lengths the radiation becomes so absorbable that the experiments have to be carried out in vacuum. The present investigation was undertaken to extend the measurements by this method to longer wave-lengths by the use of a vacuum spectrometer.

Method

The principle involved in the method is illustrated by Fig. 1. If x-rays, which have passed through slits S_1S_2, fall on the surface of the grating G at an angle of incidence θ which is within the angle of total reflection for the

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[1] A. H. Compton: Proc. Nat. Acad. Sci. **11**, p. 598 (1925).

[2] A. H. Compton: Phil. Mag. **45**, p. 1121 (1923).

[3] J. Thibaud: Revue d'optique theorique et instrumentale, **5**, p. 97 (1926).

radiation under consideration, the totally reflected x-rays will strike the plate P at R and the radiation diffracted by the grating at a point S. D is a portion of the direct beam which is used as a reference line. If λ is the wave-length of the incident radiation, α the angle between the regularly

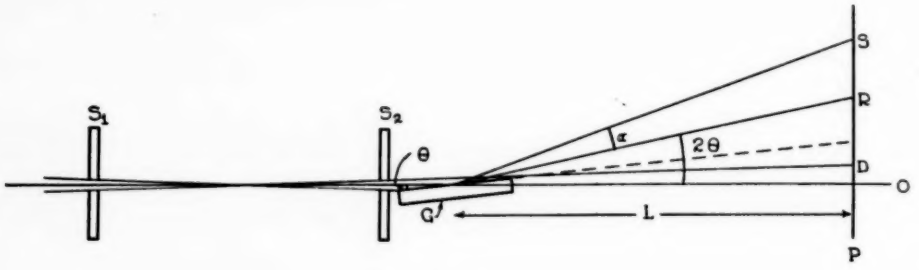

Fig. 1.

reflected and diffracted beams, d the distance apart of the lines of the grating, and n the order of the spectrum, it can be shown that

$$n\lambda = \tfrac{1}{2}d(\alpha^2 + 2\alpha\theta) \qquad (1)$$

The location of the center O of the direct image and the effective center of the grating presents some difficulty in this method since most of the direct beam is cut off by the grating. These can be found either by making a preliminary exposure before the grating is in place or by determining the relative separation of the same two lines on plates exposed at different known distances from the grating and then projecting back to the point of convergence at the grating, thereby determining the effective distance L from the grating to the plate.

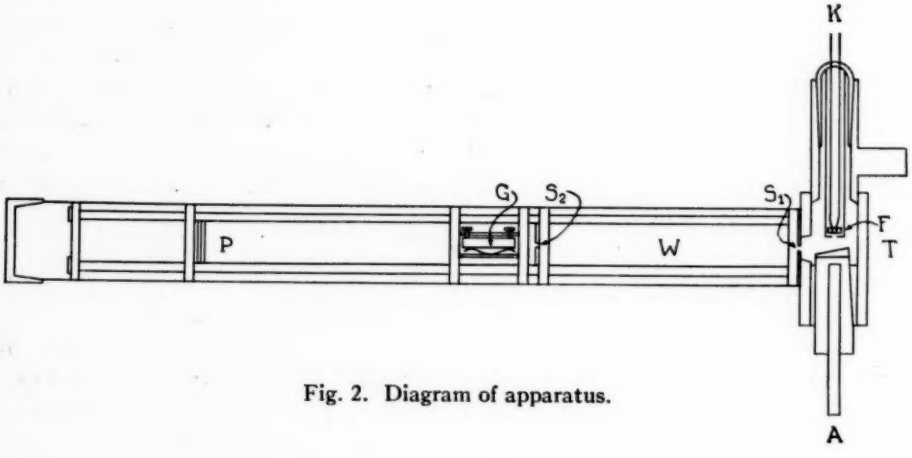

Fig. 2. Diagram of apparatus.

Apparatus

The apparatus is shown in Fig. 2. It consisted of a metal x-ray tube T with water-cooled anticathode A, and water-cooled jacket, attached directly,

with no separating film or diaphragm between, to the large brass tube W which contained the spectrometer proper. The cathode K was made of Pyrex glass with tungsten leads and an oxide coated platinum ring-shaped filament F which was heated by current from a storage battery with rheostat in circuit to control the current through the tube. Both the cathode and the anticathode were removable to make possible replacement of the filament and changing of the anticathode material. The spectrometer proper consisted of two adjustable steel slits S_1S_2, a plane grating[4] G ruled on glass (200 lines per mm, aperture 8000 lines), which was held by springs against adjustment screws to control the angle of incidence, and a photographic plate P mounted in a metal cassette. These essential parts were all mounted on a rigid metal frame which could be slid in and out of the brass tube, thus permitting adjustment of the slits and grating and the distance apart of the different members before placing the whole unit in the brass tube. Taper joints sealed with pizein wax were used throughout. The entire apparatus was pumped to an x-ray vacuum by the use of a two-stage mercury condensation pump in series with a rotary oil pump. The cassette was provided with a hinged cover, controlled from behind, which was opened after the frame holding the spectrometer parts had been inserted in the brass tube, and closed again after exposure to the x-rays, so that the cassette could be removed to develop the plate.

The slits S_1S_2 were approximately 0.5 mm wide and 20 cm apart. The grating was placed immediately beyond the second slit and adjusted so that a part of the direct beam passed by the farther edge of the grating and fell on the plate to serve as a line of reference in computing the wave-lengths. The graduations extended to within 5 mm of the end of the grating. The angles of incidence of the grating were 20′ and 40′, respectively, in the two series of measurements reported. The photographic plate was located at distances of from 10 to 30 cm from the grating. Contrast plates, developed in contrast developer, were used. These were found to give more satisfactory results than fast plates because the latter showed so much surface fogging, due to scattered x-rays, that the spectral lines were obscured. Ten kilovolts were applied to the tube. This is much in excess of the theoretical minimum required to excite the lines under investigation, but a large increase in intensity was thereby gained which offset the disadvantage of additional fogging, due to scattered radiation of shorter wave-lengths emitted at the higher voltage. It may also be noted that this latter radiation is largely eliminated by increasing the angle of incidence beyond the angle of total reflection for the radiation of shorter wave-lengths than that under investigation. The times of exposure were from twenty minutes to one hour, with a tube current of ten milli-amperes. The use of a hot, lime-coated platinum cathode insured an adequate supply of electrons at a sufficiently low temperature to prevent the presence of much ordinary light, and thus permitted the elimination of all films and screens between the anticathode and the photographic plate. This allowed the full intensity of radiation to

[4] The grating was ruled by Dr. W. Souder at the Bureau of Standards.

reach the plate and eliminated the possibility of selective absorption. Hot tungsten cathodes were tried and found to cause excessive fogging.

Results

The results are shown in Fig. 3. The effect of covering part of the plate with thin black paper is shown for the copper spectrum in the first series and for all the spectra in the second series. Only the central image *D* and total reflection line *R* due to the more penetrating part of the general radiation passed through. The spectrum lines were entirely cut off. Since the graduations extended 4 cm lengthwise of the grating and reflection took place from the entire area, the spectral lines are rather broad. This, together with the fact that the dispersion was not great, did not permit resolution of the weaker lines. The wave-lengths given in the accompanying table are, therefore, assigned to the intense $K\alpha$ lines. The chromium line was too faint for

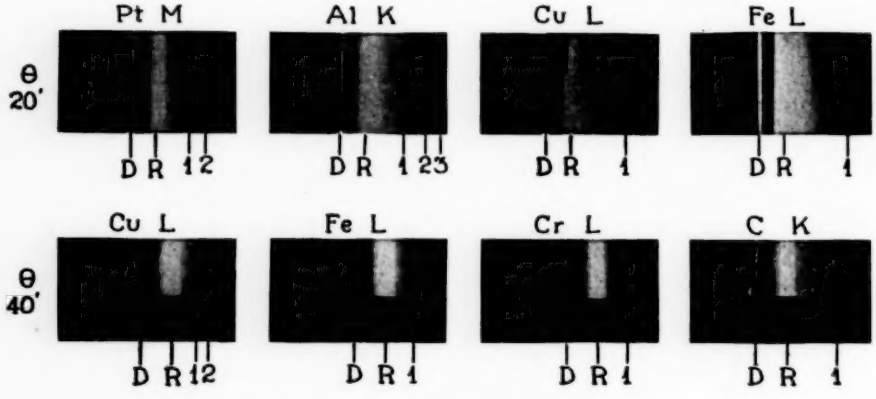

Fig. 3. X-ray spectra from a ruled grating. *D* is the direct beam, *R* the line of total reflection, 1, 2, 3 the order of the spectra.

accurate measurement. The apparatus in these preliminary experiments was arranged primarily to secure the greatest possible intensity, since the lines were all rather weak, and was not well suited to precise quantitative measurements. This was due to the width of the slits, the nearness of the plate to the grating, and the aperture of the grating which not only caused the broadening of the lines above referred to but introduced an uncertainty as to the location of the effective center of the grating. To identify the lines the wave-lengths given in Table I have been calculated by assuming the value for the wave-length of copper $L\alpha$ radiation obtained by crystal measurements; that is, 13.3A and computing from this value the corrected distance to the reference point on the plate for all the other wave-lengths. In the first series the first order $L\alpha$ line was chosen because the second order was faint, and in the second series the second order $L\alpha$. The values agree in most cases within 0.1A with those found by reflection from crystals, given in the last column.

A direct calculation of the wave-lengths was also made. For this the effective center of the grating was first determined by measuring the relative separation of the first and second order Al $K\alpha$ lines when the plate was located at 10, 20 and 30 cm from the grating for the first series; and also

TABLE I

Wave-lengths of various x-ray lines as computed from grating measurements using Cu Lα as a standard.

Element	Line	Wave-length from grating $\theta=20'$ $n=1$	$20'$ 2	$20'$ 3	$40'$ 1	$40'$ 2	Wave-length from crystals
Pt	Mα	6.0A	6.0A	5.9*A			6.0A
Al	Kα	8.4	8.4	8.3*			8.3
Cu	Lα	(13.3)†	13.5		13.1A	(13.3)A†	13.3
Fe	Lα	17.8			17.8		17.7
C	Kα				46.0		45.5

* Faint.
† Used as reference line in computing wave-lengths.

from the distance of the first order C $K\alpha$ lines from the central reference line when the plate was at 10 and 15 cm from the grating in the second series; and then projecting back to the points of convergence on the grating. The angle of incidence on the grating was determined accurately by measurement with telescope and scale. From these data the position of the center, O, (Fig. 1), can be found and the angle of diffraction α computed. The wave-lengths can then be computed by substituting the values thus obtained in Eq. (1). The results are shown in Table II. This method of computing the

TABLE II

Direct calculation of x-ray wave-lengths from grating constants.

Element	Line	Wave-lengths (Angstroms)
Pt	Mα	6.1
Al	Kα	8.5
Cu	Lα	13.6
Fe	Lα	18.0
C	Kα	45.8

center of the system is not very precise but had to be resorted to in these initial experiments since it was not convenient to locate the center by making a preliminary exposure of the photographic plate before the grating was in place.

BUREAU OF STANDARDS,
May 31, 1927.

X-RAY DIFFRACTION IN LIQUIDS: PRIMARY NORMAL ALCOHOLS

By G. W. Stewart and Roger M. Morrow

Abstract

Evidence for a molecular space array in liquid primary normal alcohols, methyl to lauryl.—The x-ray diffraction in liquids has long been known. The suggestion has been repeatedly made that the effect is caused by fragmentary crystals. The viewpoint here taken is that there is a molecular space array, not crystalline, which is named *cybotaxis*. Evidence of the cybotactic state in liquid primary normal alcohols, methyl to lauryl, is adduced. By Mo $K\alpha$ x-ray diffraction ionization curves, two significant distances are measured, the first linearly dependent upon the content of carbon atoms and the second practically independent of this change in molecular length. The latter is thus the distance of separation perpendicular to the chain, and is 4.6A with lauryl, decreasing slowly to 4.4A with butyl and then rapidly to 3.8A with methyl. The value 4.6A is in striking agreement with the work of Adam on surface films of saturated fatty acids. The increase of the first distance, linearly with carbon content, is in harmony with the work of Müller and Saville and others, in that the increase is about 1.3A per carbon atom, and leads to the conclusion that the diffraction is produced by planes containing the polar groups, which are not perpendicular to the direction of the parallel chain molecules. Comparison of peaks in the liquid and solid states show that the spacings are not the same and the phenomena is not caused by crystal fragments. The cybotactic state permits mobility, but not random motion and is peculiar to the substance. The distances computed are the most probable spacings. The molecules may be regarded as having the same orientation in a small group, too small to give optical anisotropy. The discussion does not, therefore, extend to liquid crystals but adheres to the more general condition. The conception of the cybotactic state is helpful in an understanding of solutions and other liquid phenomena. The theories of Raman and Ramanathan, Debye and Zernike and Prins are suggestive in that they indicate that a definite molecular space array is not necessary for the production of a single diffraction halo. But they in no sense negate the evidence here adduced for a cybotactic state.

I. Introduction

THE crystalline state demonstrates the complexity of the atomic forces concerning which we know but little. In the crystal there is evidently a stable space-array, the atoms or the molecules occupying lattice points and resisting deformation. But the laws underlying atomic forces can scarcely be regarded as discontinuous at the melting point. True, there is a discontinuity in position stability, but this does not require any discontinuity in the fundamental forces considered separately. As an illustration of the existence of a critical temperature, at which there is a discontinuity in stability, there may be cited the not unusual transformation from one crystal form to another. Such considerations make it difficult to accept the view, that at a certain temperature and pressure, a compound can pass from a definite space array of molecules or crystalline structure to a fluid with no semblance of space array and an entirely random motion of the molecules. In fact

other reports of experiments with x-ray diffraction in liquids have suggested the existence of a space array in liquids, but their authors have not believed the evidence of a definite space array to be convincing. Moreover, the explanations of the x-ray diffraction halo in liquids, made from other view points, have been not fully satisfactory.

The contribution of the present paper gives strong evidence for a molecular space array in the liquid primary normal alcohols, with carbon content of from one to eleven atoms. It interprets the space array observed not as caused by fragmentary crystals, but by a type of molecular arrangement wherein there is combined mobility of the component molecules and yet a recognizable space array. To this state is given the name "cybotaxis," which means "space-arrangement." The adjective is "cybotactic." A new word is necessary in order to distinguish this state from that called "crystalline."

II. The X-ray Diffraction Halo in Liquids

The diffraction halo in liquids, using the Laue spot method, was first reported by Debye and Scherrer.[1] Debierne[2] investigated the liquids mercury, methyl iodide, methylene iodide, benzene, and bromobenzene, and concluded that there need not be a simple crystalline arrangement of the atoms. Hewlett,[3] by an ionization method, found a diffraction maximum with benzene, mesitylene, and octane and suggested that these liquids have "something of a crystal structure." Keesom and Smedt[4] studied the phenomenon in liquid oxygen, argon, and nitrogen, and in carbon disulphide, benzene, water, ethyl alcohol, ethyl ether, and formic acid. They found a second ring measurable in the cases of oxygen, argon and nitrogen. Their opinion was that the effect is caused by neighboring molecules.

Wyckoff[5] experimented with liquids and liquid mixtures and concluded that the origin of the diffraction was within rather than between the molecules.

Eastman[6] compared the patterns obtained with crystalline and liquid benzene and showed a similarity.

Liquid crystals, so named because of their anisotropic optical properties, have been studied with x-rays. M. de Broglie and E. Friedel[7] have proposed that there exists for matter between the amorphous and crystalline states, two possible intermediate states of matter, "nematique" in which the molecules are distributed at random, but all have a common direction, and "smectique," in which the molecules have a common direction and are arranged in equidistant parallel layers. As will be later realized, the present contribution is not immediately concerned with optically anisotropic liquids.

[1] Debye and Scherrer, Nachr. Gesell. Wiss. Göttingen, p. 6 (1916).
[2] Debierne, Comptes rendus, **173**, p. 140 (1921).
[3] Hewlett, Phys. Rev. **20**, p. 688 (1922).
[4] Keesom and Smedt, Proc. Roy. Soc. Amsterdam **25**, p. 118 (1922) and **26**, p. 112 (1923).
[5] Wyckoff, Am. Jour. Sci. **5**, p. 455 (1923).
[6] Eastman, J. Am. Chem. Soc. **46**, p. 917 (1924).
[7] de Broglie and Friedel, Comptes rendus, **176**, p. 738 (1923).

These consist of very long molecules, and represent an extreme case of space array in liquids. Hückel[8] shows that liquid crystals do give an x-ray pattern. But this report is concerned not with the case of molecular array sufficiently extensive to give optical anisotropy, but with a more general type of array where mobility is distinctly in evidence and the molecules do not have the same direction over a volume whose diameter is large compared with the wave-length of optical rays.

III. Current Theories

The theories proposed in explanation of the x-ray diffraction halo in liquids may be regarded as successful in one respect. They have shown that the presence of a maximum does not require equidistant spacing of molecules.

Raman and Ramanathan[9] treat the fluid as a continuous substance subject to local changes in density determined by thermodynamical considerations. Their result gives a graph very much like the experimental curves of Hewlett.[3] The maximum intensity of diffraction occurs at an angle that is approximately determined by Bragg's law using the mean distance of separation of the molecules as a grating distance. This distance λ_0, lies between $0.8 \times \bar{n}^{1/3}$ and $1.0 \times \bar{n}^{1/3}$, where n is the number of molecules per $\overline{\text{cm}}^3$. Raman and Ramanathan also refer to Ehrenfest's formula quoted by Keesom and Smedt,[4] in which the interference is caused by two neighboring molecules, and to Brillouin's theory[10] based upon the quantum theory of specific heats. He shows that neither of these agree with experiment in the neighborhood of zero angle of scattering.

Debye[11] derives an approximate theory assuming that the effect is caused by neighboring molecules, and that each molecule scatters as a whole. He finds a maximum in the scattering curve which occurs at an angle defined by the quotient of the wave-length of the radiation and the diameter of the sphere assumed occupied by the molecule. He also considers the case of scattering wherein the molecule consists of two scattering centers. By this means he obtains a maximum and at larger angles, a series of maxima. Both of these theories give an angle of maximum intensity of diffraction that is of the observed order of magnitude.

Zernike and Prins[12] have just published a theory in which they consider the problem first as that of a one dimensional molecule acting as a point. Diffraction curves are computed which are like those observed in that they have a sharp maximum and very little intensity at small angles. In extending the theory to actual liquids, spherical symmetry is assumed, and the theory put in a form so that one can ascertain the effect of neighboring molecules on one another from the diffraction observations.

[8] Hückel, Phys. Zeits. **22**, p. 561 (1921).

[9] Raman and Ramanathan, Proc. Ind. Assoc. Culv. Sci. **8**, p. 127 (1923).

[10] Brillouin, Ann. d. Physique, p. 88 (1922).

[11] Debye, Jour. of Math. Phy. **4**, p. 133 (1925), (published by the Massachusetts Institute of Technology) also translated for Phys. Zeits. **28**, p. 135 (1927).

[12] Zernike and Prins, Zeits. f. Physik. **41**, p. 184 (1927).

Debye's paper does not refer to the contributions of Raman and Ramanathan, and Zernike and Prins refer to neither of the other theories. Doubtless this is because the journals containing the first two reports were not widely distributed. The chief contribution of all three theories is not that they explain the phenomena herein described, but that they indicate strongly that a maximum in the diffraction intensity *may* occur without equidistant spacing. Other than this conclusion, none of the theories has any immediate bearing upon the discussion of our results. In fact, it appears from the experiments described in this article that, for the present, the need is for experimental data to guide any future theory which must include the operation of molecular forces on anisotropic molecules.

IV. Experimental Procedure

The fluids were enclosed in very thin-walled closed cylindrical glass tubes, and when in use a tube was rotated with the axis of the cylinder coincident with the axis of the spectrometer. The x-rays from a molybdenum Coolidge tube passed successively through a slit set, the liquid mounted as described and into the ionization chamber attached directly to the second slit. The collimator and the ionization chamber slits each consisted of a Soller[13] slit set, 20 cm long, containing 8 slits each 0.079×1.6 cm in cross-section. The separating lead walls were each 0.0076 cm in thickness.

The total width of a slit set was 0.8 cm. Thus a relatively large area of the target could be utilized. Moreover, in order to obtain the optimum thickness[14] it was necessary to use cylindrical samples having diameters greater than the width of a single slit and usually of a slit set. These cylinders were rotated in order to eliminate any effect due to inequalities in the glass containers.

The ionization chamber of Allison and Clark[15] was modified by the substitution of quartz insulation for Pyrex. It was found that the insulation was entirely satisfactory and that when the chamber was once filled with methyl bromide, no serious change in content could be observed over the time of several months. The chamber was 30 cm in length. Whether or not the chamber gave relative intensity relations with the different wave-lengths, is not an important consideration in these experiments.

Observations were made in the usual manner by recording the electrometer needle velocity in scale divisions per second. The instrument was a Dolezalek pattern with a sensitivity of about 2500 divisions per volt. The corrections of observations were made as follows:

1. For the natural electrometer drift.

2. For the x-rays passing through the system without being diffracted, especially when the angle of diffraction becomes small. This correction was

[13] Soller, Phys. Rev. **24**, p. 159 (1924).

[14] I.e., thickness $= 1/\mu$, where μ is the absorption coefficient, Hull, Phys. Rev. **10**, p. 661 (1917).

[15] Allison and Clark, J.O.S.A. **8**, p. 681 (1924), refers reader for diagram to Hudson J.O.S.A. **9**, p. 259 (1924).

of importance only for chamber settings of less than 2.5° from the direction of the incident rays. It was obtained by noting the ionization current in the neighborhood of zero angle in the absence of the diffracting sample, and then by correcting this value for the absorption of the sample which was found by observation of direct transmission. In order to secure these comparisons at such high intensities, a heavy lead plate with a narrow horizontal slit was placed in front of the ionization chamber Soller slit-set. It is to be observed that these corrections are chiefly for the x-rays penetrating the walls of the slit system. One could get within 0.5° of the zero setting and yet make satisfactory corrections.

3. The diffraction curve of one of the empty glass cylinders showed a maximum at a diffraction angle of about 11°, but the slope on either side was very gradual. In fact, the correction for the glass curve appeared unimportant and was omitted.

The Coolidge molybdenum x-ray tube was operated by a transformer. Inasmuch as the primary voltage was not sinusoidal the selections of the desirable value of primary effective voltage was determined by experiment, and no direct measurement of secondary voltage was made. A sheet of zirconium oxide, obtained from the General Electric Company, absorbed about two-thirds of the $K\alpha$ radiation but gave a satisfactory isolation of this doublet, $\lambda = 0.71 \times 10^{-8}$ cm. Its success is illustrated by the diffraction curve of a non-homogeneous crystal, frozen lauryl alcohol, shown in Fig. 4. Here the width of the $K\alpha$ doublet is about 24′, in agreement with the geometry of the case.

The selection of the liquid samples was a very important matter. A space array that is not crystalline but has fluidity would surely not be easily identified. It would have a low resolving power, not only on account of the small size of a somewhat homogeneous group, but also because of the nature of the group itself. The prospect of definite results seemed to depend upon a comparison of diffraction curves obtained with molecules varying in size and shape in a systematic manner. The selection was therefore made from liquids having chain molecules, with dimensions increasing in but one direction. The primary normal alcohols were chosen because of their availability. The molecule is generally believed to consist of a chain of carbons, each laterally bonded to two hydrogen atoms, and the chain terminated at one end with H and at the other end with OH. Thus the increase in length can be made by the addition of CH_2. Our experiments are in accord with this description. In the tests this addition of CH_2 was made ten times, the samples covering all the normal alcohols from methyl, CH_3OH, to lauryl, $C_{11}H_{23}OH$. Nine of these were obtained from the laboratories of the Eastman Kodak Company. Decyl was supplied by Fritsche Bros. Inc. Ethyl was prepared by Mrs. Roger M. Morrow.

V. Experimental Results

Nature of radiation. That the zirconium screen isolated the $K\alpha$ doublet satisfactorily was proved by tests on a crystal powder. The unseparated

doublet was the only observed characteristic radiation, but the general radiation was confusing and had to be virtually, though not actually, eliminated. This was accomplished by the use of an appropriate voltage. Fig. 1 shows the change of an alcohol diffraction intensity curve with alteration of the voltage. The principal maxima are plotted to the same scale but with displaced ordinates. The curves are designated by the primary voltages on the transformer. It is apparent that the peaks at approximately 2°, 5° and 9°, are not caused by the same radiation, for the alteration of voltage seriously modifies the relative value and position of one of the three.

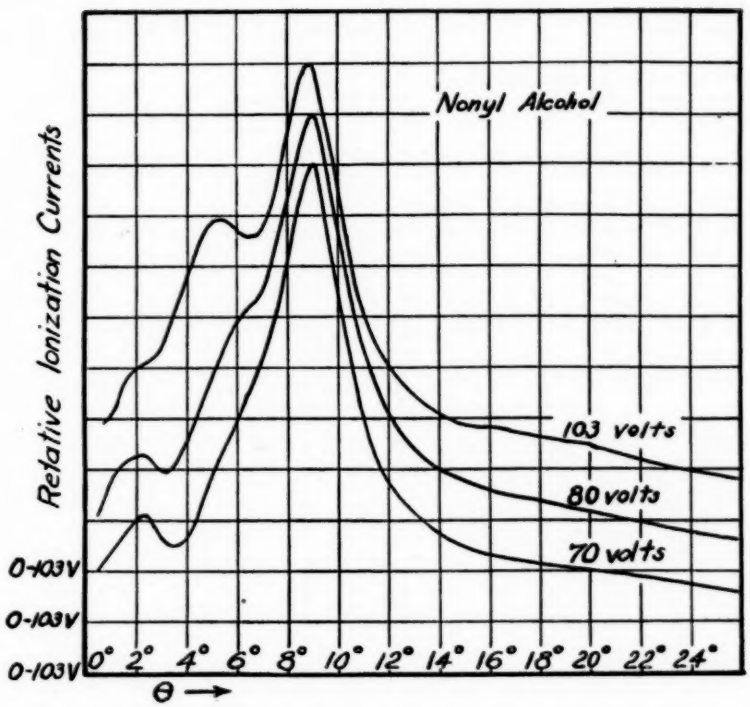

Fig. 1. Intensity-diffraction curve with variation in primary voltage.

This peak is thus identified as caused by the general radiation. Our knowledge of the commercial circuit alternating current was not sufficient to check the position of this peak. An approximate check (see Siegbahn's Spectroscopy of x-rays p. 208) indicates that the peak with 103 volts, r.m.s. primary, and 46.3 K.V. maximum secondary should be at about 0.39A. Assuming the peak 8.9° to be produced by the .71A radiation, the diffraction angle of 0.39A should be at 5°. The variation in absorption of the zirconium screen would, of course, shift the peak to smaller angles. The observed position of the central peak is in accord with the interpretation that it is caused by the general radiation.[16]

[16] A test of absorption was made by means of a 2 mm aluminum screen and it was found that the absorption of the 9° peak was 95 percent and the 5° peak was 50 percent. These values are consistent with the interpretation of the former as 0.71A and the latter of 0.44A.

Fig. 1 also shows that the same radiation, i.e., 0.71A, is responsible for the peaks at 2.2° and 8.9°. The important conclusions from Fig. 1 are (1) that 70 volts, effective value, on the primary partially avoids the confusion caused by general radiation, and (2) that two peaks are caused by the same radiation, 0.71A.

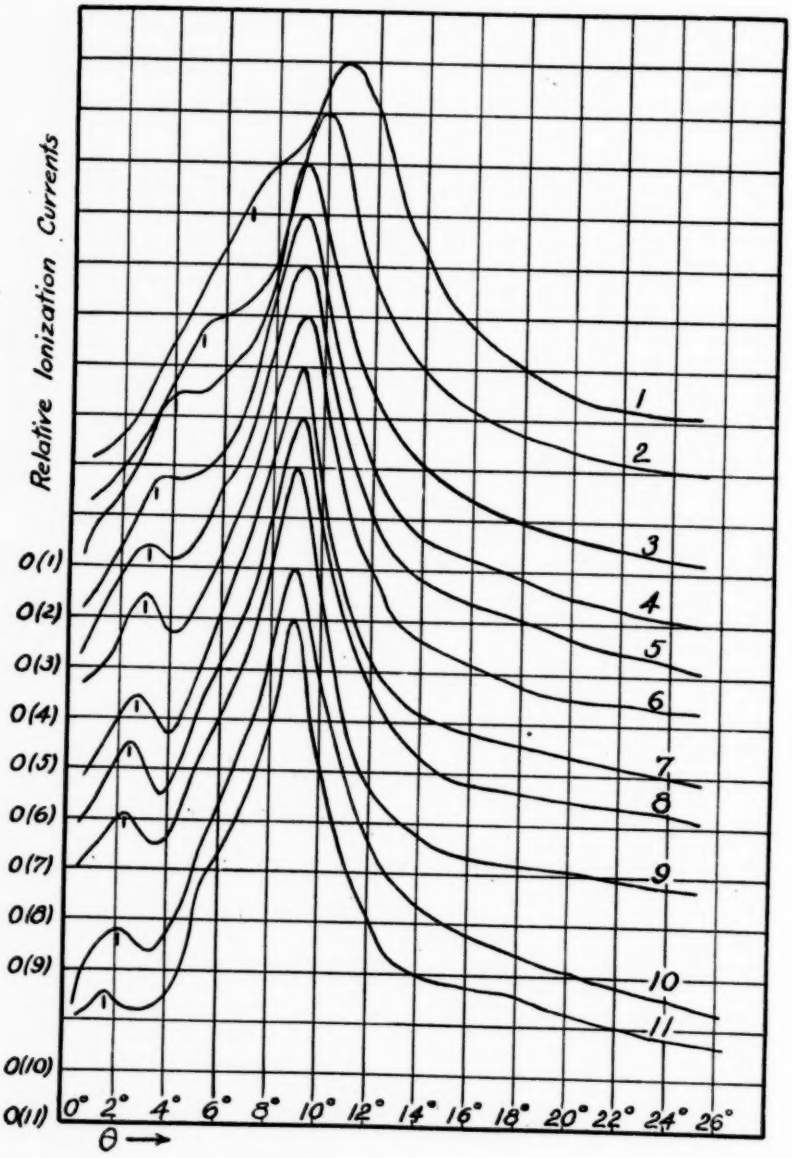

Fig. 2. Intensity-diffraction curve with normal alcohols containing from one to eleven carbon atoms.

Variation of diffraction with increasing content of CH_2. In Fig. 2 are shown the diffraction curves for the normal alcohols from methyl to lauryl, in-

clusive. In order to show all of them in one figure the ordinates are displaced as indicated by the zero ordinates shown on the left. The voltage on the primary was 70 effective volts. The curves are designated by numbers which indicate the content of carbon atoms in the molecule. Each curve is a mean of three. For some of the peaks more than three curves were averaged.

Computed "planar" distances. Fig. 3 shows the angular positions of the peaks and the corresponding planar distances computed by the formula, $0.71 = 2d \sin(\theta/2)$ where θ is the angle of diffraction.

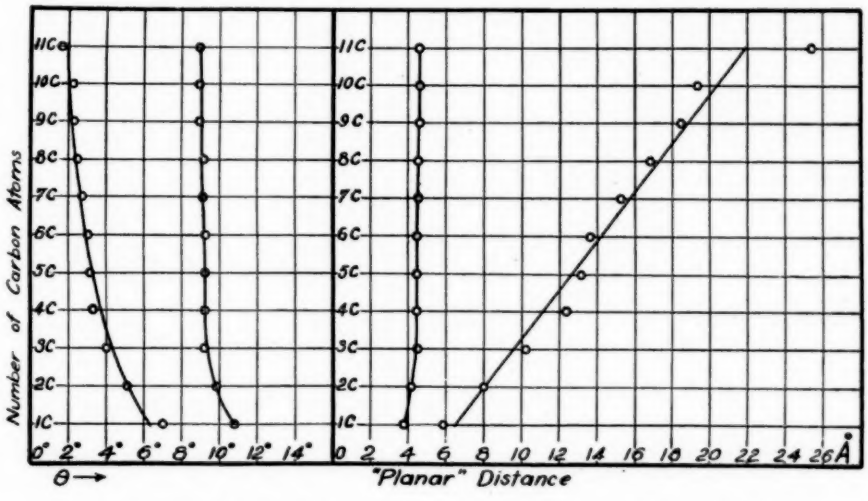

Fig. 3. Variation of diffraction peaks and "planar distances" with content of carbon atoms in the molecule.

Comparison of solid and liquid states. In order to shed light upon the physical condition in the liquid state, curves for lauryl alcohol, $C_{11}H_{23}(OH)$, shown in Fig. 4, were taken with the liquid and the solid. The liquid was at 21°C and the solid at practically its melting point 19°C.

VI. Discussion of Results

Inter-planar distances. The term "inter-planar" is used not with the sense that there is a fixed orientation of molecules determined by planes, but merely as referring to inter-planar distances determined by Bragg's law. The experiments clearly show, as in Fig. 3, the variation of two such distances, d_1 and d_2, and that the cause of the large variation in d_2 is not the same as the cause of the small variation in d_1. The former is linear and the latter is not. Since the variation in d_2 is linear, about 1.54A for each CH_2 addition (see below) the accepted shape of the molecule as a "chain" leads to the conclusion that d_2 is determined by the length of the molecule. Since d_1 is not altered linearly, it must be caused by the separation of molecules measured perpendicularly to their lengths. Moreover d_1 would, on account of molecular symmetry, probably represent two distances, approximately alike. It appears from Fig. 3 that d_1 approaches a limiting value for further addi-

tions to the molecular length. Of course the curve should not be extrapolated, *but if the further additions of CH_2 merely lengthen the molecule, 4.6A may be accepted as the mean distance, or most probable distance between adjacent long chain molecules made up of CH_2.* That this agrees with other measurements, will later be mentioned.

Length and arrangement of molecules. The above shows that, while 4.6A may be interpreted as the distance of separation of the molecules, the other inter-planar distance may or may not be the length of the molecule. There are two reasons for believing that it is not. In the first place, the alcohol molecule is strongly polar, the active group being OH. It is probable that in any alignment of the molecules in the direction of molecular length, these polar groups would be together. In the second place, approximate computa-

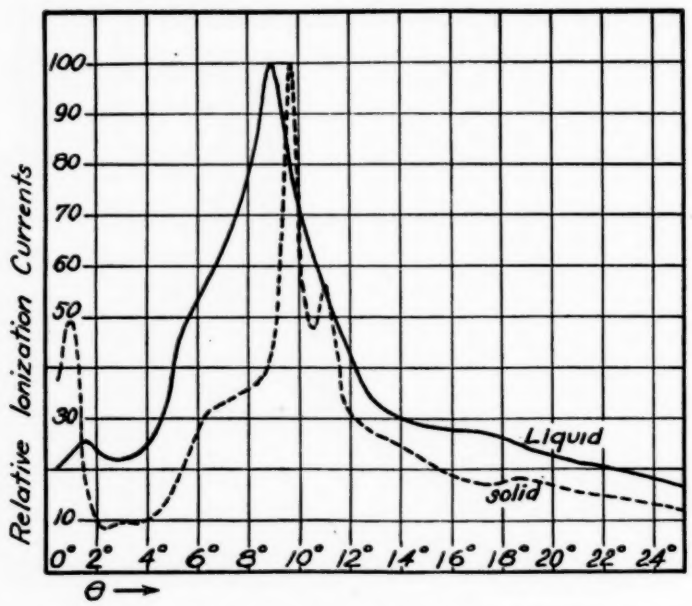

Fig. 4. Diffraction curves of solid and liquid lauryl alcohol.

tions of density from the above planar distances give evidence for this arrangement of molecules. Consider first that the distance d_2 is caused by the spacing occasioned by one molecule only and (as is assumed throughout) that in the plane perpendicular to this length, the molecules are arranged at the corners of squares. Then the density would be $\rho = 1/d_1^2 \times 1/d_2 \times$ (molecular weight) $\times$ (mass of H atom). Substituting respectively the values 4.6×10^{-8}, 20.4×10^{-8}, 158, and 1.66×10^{-24}, ρ becomes 0.60. But this density is much too small, the correct value being approximately 0.83. If d_2 be assumed caused by two molecules, as suggested in the preceding paragraph then the density 0.60 would be doubled. Assume the molecules to be aligned as above indicated, but let the polar groups occur in pairs along any line of molecules. If these pairs be now shifted so that they are in planes forming equal intercepts on three rectangular axes, one of which is in the

direction of the molecular lengths, then the distances from one pair to any of its neighbors in any of these planes is constant. Two neighboring pairs are not immediately adjacent, or at a distance d_1, but at a distance $2^{1/2} \times d_1$ from one another. With this arrangement the distance between two planes is $0.576 \times 2a$, where a is the length of a molecule. For decyl alcohol, for example, a is 10.2A/0.576 or 17.6A. If the density of decyl be now computed as above, it is 0.70. Of course by adjusting the planes at a different angle an arrangement can be found that will give the actual density, but if assumed as already stated the result is strikingly in accord with several other facts as will now be explained.

Adam[17] experimented with films of saturated fatty acids on the surface of water. His experiments were with carbon chains ranging from twelve to twenty-six carbons. These differ from the alcohol chains only in that the polar group at the head in the water is COOH instead of CH_2OH. It was found that with the films on water, the area occupied by one molecule, oriented perpendicularly to the surface, was 21.0×10^{-16} cm^2, and that this value was independent of the nature of the acid. If, however, he used a solution of HCl, $N/100$, the corresponding area was 25.0×10^{-16} cm. The interpretation at present accepted is that in the latter case the polar groups are adjacent, and in the former they are alternated in position vertically in such a manner that the polar groups are not side by side. *It is most interesting to note that the area, 21.0×10^{-16} cm^2 is precisely $(4.58 \times 10^{-8}$ cm$)^2$. Hence the surface film measurements agree with our determination of d_1 or 4.6×10^{-8}, and the relatively displaced positions of the polar groups occur in both cases.* This comparison may be said to give confirmatory evidence of the correctness of the interpretations given in the two widely different cases, the surface film and the liquid interior. This area of cross section of a CH_2 group is also confirmed by estimations made in other ways. It is thus with great confidence that the distance 4.6×10^{-8} cm is to be accepted as the planar distances between the molecules in the liquid.

Each CH_2 group adds to d_2 one-half of 1.54A or 0.77A. This represents an increase in a of 0.77A/0.576 or 1.33A. This is the longitudinal separation of C atoms in the chain and is of the proper order of magnitude.

A comparison should also be made with the experiments of Müller and Saville[18] on long chain hydrocarbons in the solid state. There they found the addition per C atom to be 1.3×10^{-8} cm or approximately the same as in the liquids. This reference is only to one of several experiments in which this change in length with C atoms is of the same order. The correspondence between the solid and liquid experiments gives greater confidence in the interpretation of both.

Another interesting confirmatory point is the alteration of density of the alcohols. The formula for density is obtained by dividing the molecular weight by the volume occupied by a molecule, or the length of the molecule

[17] Adam, Proc. Roy. Soc. **99A**, p. 336 (1921); **101A**, p. 452, p. 456 (1922); **103A**, p. 676, 687 (1923).

[18] Müller and Saville, Journal Chem. Soc. **127**, p. 599 (1925).

times d_1^2. The length of the molecule is found from the above interpretation of arrangement to be 4.32A plus $n \times 1.33$A where n is the number of carbon atoms. Hence the entire formula for density will be $\rho = (18+14n) \times 1.66 \times 10^{-24} [(4.32+1.33n)\, d_1^2 \times 10^{-24}]^{-1}$. The values computed for eleven of the alcohols are compared in Table I with the known values of density. It is to be noted as a matter of interest that if the computed values are regarded as 20 percent in error, because of the inaccuracy of the approximate arrangement described, then the final computed values, with one exception, agree within less than 5 percent with the values of density known for 20°C. Propyl is 9 percent in error. The purpose of the exhibit in Table I is to show a consistency in the interpretation and only to this extent is the evidence confirmatory.

TABLE I

Densities of alcohols.

alcohol	computed ρ	actual density	1.2ρ
Methyl	0.653	0.792*	0.783
Ethyl	.625	.789*	.747
Propyl	.612	.804*	.734
Butyl	.654	.810*	.784
Amyl	.680	.817*	.816
Hexyl	.702	.820*	.842
Heptyl	.714	.817‡	.856
Octyl	.718	.827*	.861
Nonyl	.710	.828*	.852
Decyl	.709	.830*	.850
Lauryl	.714	.833*	.856

* At 20°C, ‡ at 22°C given by International Critical Tables.

The arrangement of molecules discussed, the computations in accord therewith, and the comparison with other evidence, should be regarded as convincing evidence of the cybotactic state.

Structure not crystalline. There are several reasons that lead to the rejection of the theory of fragmentary crystals[19] in liquids as the basis of explanation in the alcohol experiments. First, the crystal theory does not agree with our general views of the two states, solid and liquid. One can understand that the solid state may depend upon a critical temperature or melting point, but it is not clear why, under the same view, any fragments of crystal should remain. A second objection to the fragmentary crystal theory is such experimental evidence as is shown in Fig. 4. The position of the diffraction peaks in solid lauryl alcohol are at 1.0°, 9.7° and 11.0°, and in the liquid are at 1.65° and 8.8°. Obviously, the computed grating spacings are not the same. Stated in the same order, they are, 35.6, 4.2, 3.7; 24.7, 4.6, in Angstrom units. One of the distances has been increased by melting and the other decreased. The structure in the solid and in the liquid may have similarity, but they cannot be the same. Hence, the groups in the liquid are not merely fragments of the crystals in the solid. As a third aspect, con-

[19] See Hewlett, ref. 3, Hückel, ref. 8, and A. H. Compton, Bull. Nat. Res. Council, No. 20.

sideration should be given to the resolving power of fragmentary crystals. The literature [20] provides a formula for the breadth of a line in terms of the wave-length and size of the crystal fragment. It is $h=2(\ln 2/\pi)^{1/2}\lambda/\Omega(\cos\theta/2)^{-1}$ wherein h is the breadth of peak half way from base to maximum, λ is the wave-length, Ω is the length of edge of the cubic crystal. The value of h in lauryl, for example, can be obtained from Fig. 2. It is 3° at $\theta=8.8°$ giving Ω a value of about 14×10^{-8} cm. Inasmuch as this is less than the length of one of the spacings, one is not encouraged to find the explanation of the peak breadths in the size of the supposed crystal fragments. Even the assumption that there are two distances concerned instead of one, would not essentially modify this view.

The discussion above given concerning the arrangement of the molecules is presented, not as proof, but merely as an indication of the essential correctness of the view of the cybotactic state here put forth. *The important conclusion is that a space array exists* and that it depends upon the carbon content somewhat in the manner indicated.

Absence of second order. In the present experiments second order maxima are not found. This is not surprising. If diffraction does not occur in crystals but in an oriented state not so fixed in form, the second order would probably be relatively less in intensity than with crystals. A careful effort has not been made to detect the second order, but it certainly is less than 5 percent of the first order. Fig. 2 suggests that with lauryl a sharper peak and a trace of second order exist. Only the former seems certain at the present stage of the experiments.

Surface Effect. One might readily conceive of the cybotactic state as caused by the presence of the surface of the glass cylinder in which the liquids are placed. That this is not true was shown by varying the diameter of the cylinder three-fold, yet with the beam narrower than the diameter. In each case the surface exposed to the x-rays was approximately the same. But the observations showed that the diffracted beam altered with the volume, and in a manner to be expected from computations of optimum thickness. Moreover, the relative magnitudes of the two diffraction peaks remained approximately the same with the variation in diameter. From these observations, the hypothesis of a surface phenomenon as responsible is untenable.

Cybotatic state. As indicated in the introduction to this paper, one cannot readily accept the view that the atomic and molecular forces undergo discontinuities at the melting point. But the resulting stability may be critical at this temperature. The molecular arrangement that was stable in the crystalline form may approximate the most probable grouping in the liquid state. In the former there is rigidity of form, but in the latter there is mobility. In both the molecular vibrations are those of acoustic waves. Throughout the liquid at any instant there are scattered many small groups having the spacings reported herein. Over any appreciable time, there are a greater number of these groups than of groups having spacings of any other adjacent values. These groups do not retain their identity. Our diffraction

[20] P. Scherrer. Nachr. d. Konig. Gesell. d. Wiss. at Göttingen, 1919–19, p. 98.

curves have broad peaks not only through the minute size of these groups but also because there is a wide distribution of values of the distances among the organized groups. The above description regards the latter as the more important factor in the diffraction result.

An attempted discussion in detail of these molecular groups would be premature. Nevertheless it is important to point out the similarity of the breadth of the chief peak of the diffraction curves of the alcohols from hexyl ($C_6H_{13}OH$) to lauryl ($C_{11}H_{23}OH$). The breadth cannot be determined by the size of the group, for it would seem that the doubling (almost) of the molecular length would materially change the size of a group. But the evidence of our results taken in entirety points to the inapplicability of resolving power as dependent upon size. The positions of the molecules are not sufficiently stable to apply a crystalline theory.

It is important that a differentiation between the cybotatic and the crystalline states be definitely drawn. Each refers to an organization of molecules. In each the organization depends upon the nature of the molecules as expressed in molecular forces. But one is fluid and the other solid. The analogy between the two does, however, give a clear conception of the nature of a solution. We know that in solid alloys, the atoms of the alloying material participate in the crystal lattice of the metal alloyed. It is a solid solution. *In a liquid solvent, the solute is "dissolved" in that it participates in the organized grouping of the solvent.* If it does not so participate it is a foreigner and might be called a *colloid*. This suggestion gives a helpful conception of a solution.

Universality of cybotaxis in liquids. A general conclusion of the universality of cybotaxis in liquids is not justified, but certainly the hypothesis is a very attractive one. It is noticed that, as the molecule becomes shorter, its group organization, as shown by the width of the 4.6A peak in Fig. 3, follows a more widely distributed probability. In fact the diffraction curve more and more resembles that of water as the molecule becomes more nearly the shape of that molecule. Our present x-ray method does not show the cybotatic state clearly unless it becomes strongly marked by the use of long chain molecules. Nevertheless, cybotaxis appears to be of importance with any liquid. This is indicated by latent heat of vaporization values.

A large portion of the observations in this paper were made by Mr. Wm. D. Crozier, the research assistant of the first named author. His splendid aid is gladly acknowledged.

This study of liquids is being continued with acids, with paraffins, and with various isomers.

PHYSICS LABORATORY,
UNIVERSITY OF IOWA.
June, 1927.

AN EXPERIMENTAL STUDY OF THE RELATIVE INTENSITIES OF X-RAY LINES IN THE L-SPECTRUM OF THORIUM

By Samuel K. Allison

Abstract

The relative intensities of the thorium L-series lines have been measured at 31.8 kilovolts using an ionization chamber spectrometer. In addition to the lines previously reported by other investigators, the lines Th$L\eta$, Th$L\beta_7$, Th$L\gamma_2$ were found. No indications of Th$L\gamma_5$ or Th$L\gamma_4$ could be found. The relative intensities have been corrected for absorption in the mica windows and air in the path from x-ray tube to ionization chamber, and for the fraction of the radiation absorbed in the methyl iodide in the ionization chamber. It was found that in the voltage range between the critical excitation voltage V_0 and 31.8 kilovolts, the intensity of Th$L\alpha_1$ or Th$L\beta_{1,5}$ at any voltage V could be expressed by $I=k(V-V_0)^2$ within the limits of experimental error. Using this expression the relative intensities at 31.8 kilovolts were extrapolated to the relative intensities at high voltage, to which it was assumed the theoretical predictions apply. The intensity rules for doublets hold for lines involving the levels L_{21} and L_{22}. The predictions of Wentzel based on Schrödinger's new quantum mechanics for the relative intensities of "sharp" and "diffuse" series doublets are confirmed, but the experimental intensities of the "principal" series doublets are too low by a factor of 7. They are also too low in the measurements of Jönsson on tungsten. The results obtained are as follows:

Line	l	α_2	α_1	η	β_6	β_2	β_7	β_1	β_3	γ_5	γ_1	γ_2	$\gamma_3+\gamma_8$	γ_4
Rel. Int. (32 kv.)	3.6	12	100	1.1	1.4	26	.45	38	1.8	0	8.5	.81	3.1	0
Rel. Int. (high voltage)	3.6	12	100	1.8	1.4	26	.45	62	3.3	0	14	1.5	5.3	0

Introduction

THE first estimates of the relative intensities of x-ray lines in the L-series were made by the visual observation of photographic plates. The observations of Coster[1] are particularly interesting. More precise measurements were made by Duane and Patterson,[2] and Allison and Armstrong[3] using an improved form of the Bragg ionization chamber method.

A fundamental problem in attempting to measure relative intensities of x-ray lines by the ionization currents produced in a gas is the question of the relative efficiency of different wave-lengths in producing gaseous ions. In an attempt to avoid this difficulty, Jönsson[4] has replaced the ionization chamber by a Geiger point-counter. It does not seem, however, that this

[1] Coster, Phil. Mag. **43**, 1070 (1922) see especially page 1087.

[2] Duane and Patterson, Proc. Nat. Acad. Sci. **6**, 518 (1920); *ibid.* **8**, 85 (1922).

[3] Allison and Armstrong, Phys. Rev. **26**, 714 (1925).

[4] Jönsson, Zeits. f. Physik. **36**, 426 (1926); Zeits. f. Physik. **41**, 221 (1927). Since the subject matter of this paper is directly concerned with the first of the above papers by Jönsson, future reference in this article to the work of Jönsson will, unless expressly stated otherwise, refer to the first of these paper.

procedure has really avoided the main difficulty. For it is certainly true (speaking in the language of the corpuscular theory of x-rays) that not every quantum which enters the chamber of the point-counter produces a discharge, and it remains to be proved that the fraction of those entering to which the discharges are due is not a function of the wave-length. Nevertheless the fact that the measurements of Jönsson are in good agreement with those of Duane and Patterson, and Allison and Armstrong, seems to support the claims of both methods to give real measurements of relative *intensities* of x-ray lines. This question will be discussed again in a later section of this paper.

The measurements of Duane and Patterson and of Allison and Armstrong covered the relative intensities of lines in the γ, β, and α groups of the tungsten L-spectrum, but did not attempt to compare intensities of lines in different groups. This was first accomplished by Jönsson in tungsten and platinum. In as far as the measurements of Allison and Armstrong and those of Jönsson on tungsten can be compared, the agreement is fairly good. In one instance, the difference between the values reported seems to be outside the experimental error, namely the relative intensities of $L\gamma_3$ and $L\gamma_2$. Allison and Armstrong found 100:63, Jönsson 100:74. The reason for this is not yet clear. The difference between the reported values of $L\beta_3$ to $L\beta_4$ seems to be due to high absorption in the experiments of Allison and Armstrong, as suggested by Jönsson.

Apparatus

(1) *Generating set.* 500-cycle alternating current was produced by a 2 kilowatt motor generator run on the laboratory storage battery circuit. The field current of the generator was supplied by the laboratory storage battery and regulated by appropriate resistances. The 500-cycle current went through the primary of an x-ray transformer, and the high potential 500-cycle current from the secondary was rectified by two kenotrons and stored up in a condenser which discharged through the x-ray tube.[5] The capacity (0.011 m.f.) was such that at the operating conditions (7.5 m.a. and 32 kv) the calculated voltage fluctuations were about 2.1 percent.

(2) *Voltage measurements.* The primary voltage on the high-potential transformer was read on a voltmeter with 0–240 volt scale. A rough indication of the voltage used on the x-ray tube was obtained from a General Electric attracted disc electrostatic voltmeter. Whenever in the course of the work it was essential to know the working voltage accurately (as in the measurement of the intensities of the lines as a function of voltage) the voltage was determined from the limit of the spectrum by the Duane-Hunt law (at the tube current and primary voltage used) and then the desired experiments were immediately performed. The measurement of high voltages by the Duane-Hunt law is probably as accurate a method as we now have for such work. The fluctuations in the root-mean-square voltage on the primary of the transformer were less than 0.5 percent.

[5] A. W. Hull, Gen. Elect. Review, **19**, 173–81 (1916).

(3) *The x-ray tube.* The design of the x-ray tube is shown in Fig. 1. The tube was constructed of Pyrex glass. The cement used in attaching the removable metal parts was a high-vacuum cement with a chicle base, supplied by the Research Laboratories of the Westinghouse Electric Company. It proved to be very satisfactory. The metallic thorium used was obtained from the Westinghouse Lamp Works through the courtesy of Dr. C. T. Ulrey. It was in the form of a disk about 1 mm thick and 5 mm in radius. By working rapidly it was found that this could be spot welded to the face of the water-cooled copper target. The welds thus obtained were not highly perfect but nevertheless proved satisfactory. After welding, the face of the metallic thorium was filed down to a smooth surface. The portion of the radiation used in the spectrometer left the target at a glancing angle of 45° and went through a mica window 0.001 cm thick.

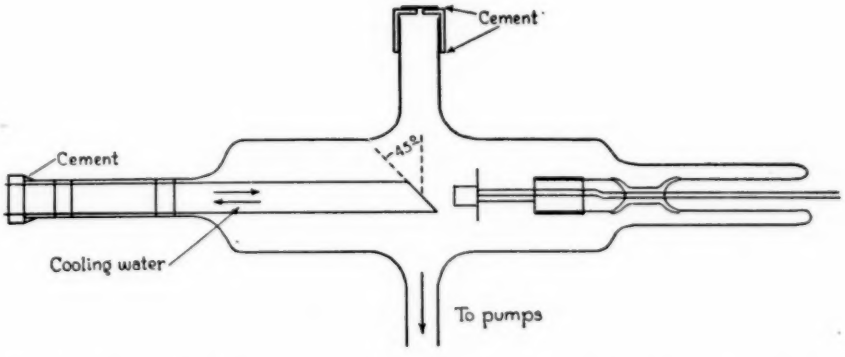

Fig. 1. X-ray tube with water-cooled copper target and mica window used in relative intensity measurements.

(4) *The spectrometer.* The spectrometer was a converted optical instrument. Settings of the calcite crystal could be made to 30″ of arc. The slits of the spectrometer were 42 cm apart and the width of each slit was 0.18 mm, making the angular breadth of the beam a little less than 3′ of arc. The ionization chamber resembled closely those used by Duane[6] except that the window through which the radiation entered was of mica 0.001 cm thick, and the insulated electrode entered the chamber through an amberoid plug. The chamber was 32 cm long. The gas used in the chamber was methyl iodide. The ionization currents were measured with a Dolezalek electrometer and a lamp and scale arrangement giving a sensitivity of about 2.5 meters per volt.

Measurements of New Wave-Lengths in the Thorium L-Spectrum

In the course of the work several lines were found in the spectrum whose presence is called for by the energy level diagram and the selection principles but which have not been reported by previous investigators. These lines are all weak. A rough prediction of their wave-lengths was obtained from

[6] J. C. Hudson, J. Opt. Soc. Am. and Rev. Sci. Inst. 9, 259 (1924).

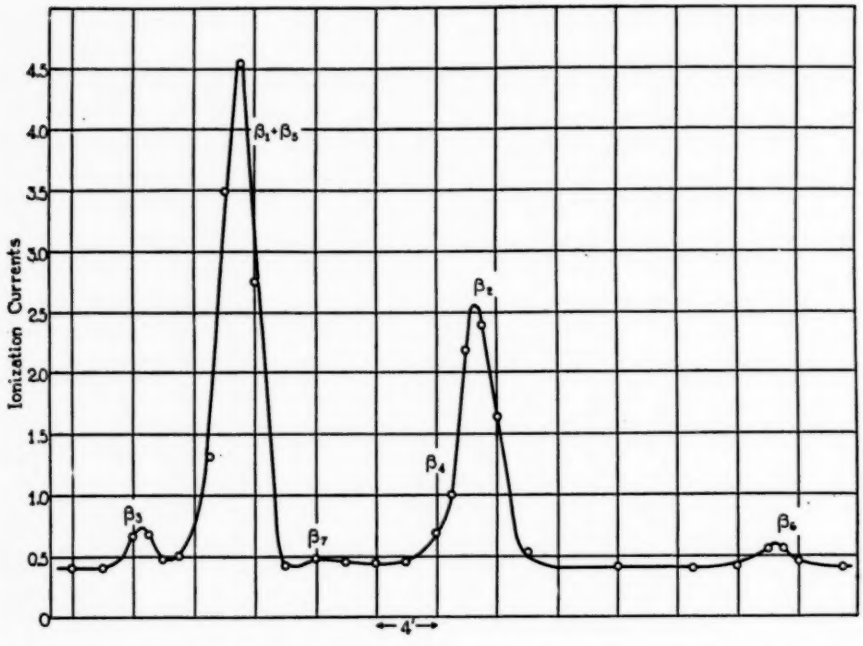

Fig. 2. Lines in the thorium $L\beta$ group. This curve is one taken merely for the purpose of locating the lines on the angular scale of the spectrometer, but gives a reliable indication of the relative intensities.

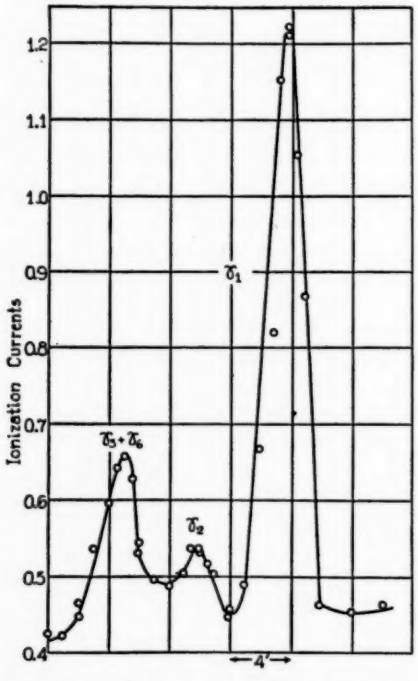

Fig. 3. Thorium $L\gamma$ group. In order to avoid a false impression of the intensity of these lines with respect to the general radiation it should be pointed out that the base-line of intensities is not that of zero intensity.

the energy level diagram for thorium given by Siegbahn in his "Spectroscopy of X-rays." The ν/R values of N_6, N_5, O_5, $O_{4,3}$ were estimated by interpolation. The following table gives the calculated and observed wave-lengths of the new lines. The spectrometer was not suited to wave-length measurements of high accuracy.

TABLE I

New wave-lengths in the thorium L-series.

Line	Calculated	Observed
η	852 (X. U.)	854 (X. U.)
β_7	772	772
γ_2	642	641

METHOD OF MEASUREMENT OF INTENSITIES

The intensity of a line was taken as proportional to the height of the tip of the peak above the base-line of the general radiation. In the case of the lines γ_3 and γ_6 which were not separated, the intensity of the combined lines relative to γ_1 was measured by comparing the products of the maximum ordinate by the half-breadth of the peak. This method has also been used by Jönsson in his second paper on intensities in the L series.

CORRECTIONS TO THE OBSERVED INTENSITIES

In order to obtain the relative intensities of the lines in the spectrum at some given voltage, the observed intensities must be corrected for relative absorption. The sources of this absorption may be listed as follows: (1) Absorption in the target itself due to generation of x-rays below the surface; (2) Absorption in the film of tungsten over the target due to the sputtering and vaporization of the tungsten filament; (3) Absorption in the mica windows and in the air path from the tube to the ionization chamber; (4) Absorption in the calcite crystal; (5) Correction for the fraction of the radiation absorbed in the ionization chamber.

(1) No correction was made for the absorption in the thorium target itself. It is believed[7] that for radiation leaving the target at 45° and voltages not above 2–3 times the critical voltage, this correction is very small for a smooth metallic target.

(2) No correction was made for the absorption in the film of tungsten over the target face. If this film is 10^{-5} cm thick the correction for the lines γ_1 and α_1 is of the order of 5 percent, which is of the order of the experimental error. To avoid this difficulty, Jönsson has used oxide coated platinum filaments. It seems to be difficult to obtain steady operating conditions with coated

[7] The order of magnitude of this correction is difficult to estimate. Webster and Hennings (Phys. Rev. **21**, 301 (1923)) found evidence that there was a mean depth of production of x-rays in a molybdenum target at 30 kv. of 1.4×10^{-4} cm. This depth would probably be less for Th, but very little is known about the absorption coefficient of Th for its own L-radiation. Very rough guesswork places the correction to the L-lines most widely separated in wave-length as 3 to 4 percent.

filaments. Fortunately there are no coincidences in wave-length in the tungsten and thorium L-spectra.

(3) The correction for absorption in the air path and mica windows was calculated from the absorption coefficients for air given in Siegbahn's "Spectroscopy of X-rays," and for mica by Unnewehr.[8] The length of path in air was 58 cm; in mica 0.002 cm. The extent of the correction applied is shown in the table at the end of this section.

(4) No correction was made for the absorption of the radiation in the reflecting crystal. Experiments on this point by Davis and Stempel[9] and by Wagner and Kulenkampff[10] have shown that for calcite the percent of the incident monochromatic radiation reflected is practically independent of the wave-length throughout this range.

(5) For the harder lines of the thorium L-series, an appreciable fraction of the radiation passed through the methyl iodide vapor without being absorbed. It was assumed that the intensity of the radiation was proportional to the ionization current caused by that fraction which is absorbed. This has been shown to be true for air by the experiments of Kulenkampff.[11] Glocker[12] has stated that this is true for all gases if the radiation has wave-lengths sufficiently far removed from the critical absorption wave-lengths of the gas.

In order to make this correction it was necessary to know the pressure of the methyl iodide vapor in the ionization chamber. The methyl iodide in liquid form contained in a Pyrex glass bulb was attached to the ionization chamber and then was frozen by immersion in liquid air. The air in the ionization chamber was then pumped out and as the methyl iodide was allowed to return to room temperature its pressure in the chamber could be measured on a manometer. It was found that best results could be obtained with a pressure of 24 cms. This corresponds to a density of 1.65×10^{-3} grams of iodine per cc. The mass absorption coefficient of iodine for wave-length 1A was assumed to be 104, and to vary with the cube of the wave-length throughout the thorium L-spectrum. The length of the ionization chamber was 32 cm. Since the absorption of the line Th$L\alpha_1$ was practically complete, the correction to be applied to any other line of wave-length λ could be obtained from the expression

$$1/(1-e^{-\mu_\lambda t})$$

where μ_λ is the absorption coefficient for the wave-length λ. The resultant corrections from this formula are shown in the table at the end of this section. The fraction of the radiation transmitted by the methyl iodide vapor was scattered and absorbed in the glass wall at the rear of the ionization chamber. No correction was made for this contribution to the ionization current.

[8] Unnewehr, Phys. Rev. **22**, 529 (1923).
[9] Davis and Stempel, Phys. Rev. **17**, 608 (1921).
[10] Kulenkampff, Ann. d. Physik. **68**, 369 (1922).
[11] Kulenkampff, Ann. der Physik. **79**, 97 (1926).
[12] Glocker, Zeits. f. Physik. **40**, 479 (1927).

TABLE II

Absorption corrections.

Line	λ (X. U.)	μ for air (t = 58 cm)	μ mica (t = .002 cm)	Correction factor for absorption outside chamber	μ for iodine (t = 32 cm)	Correction factor for absorption inside chamber	Total correction for absorption
l	1112	5.3×10^{-3}	36	1.17	23×10^{-2}	1.00	1.17
α_2	965	3.7	20	1.02	16	1.00	1.02
α_1	953	3.6	19	1.00	15	1.00	1.00
η	852	2.8	15	.95	11	1.03	.98
β_6	826	2.5	14	.94	10	1.05	.98
β_2	791	2.3	13	.92	8.6	1.07	.98
β_7	772	2.1	12	.90	7.9	1.09	.98
$\beta_1+\beta_5$	763	2.1	12	.90	7.6	1.10	.99
β_3	752	2.0	11	.90	7.3	1.11	1.00
γ_5	(673)	1.5	8.5	.88	5.1	1.24	1.09
γ_1	651	1.4	7.8	.86	4.8	1.27	1.10
γ_2	640	1.4	7.5	.86	4.5	1.32	1.14
$\gamma_3+\gamma_6$	632	1.3	7.4	.86	4.3	1.34	1.16
γ_4	(608)	1.2	6.7	.86	3.9	1.42	1.22

VARIATION OF THE INTENSITIES OF THE LINES WITH VOLTAGE

Because of the existence of three critical excitation potentials in the L-series, the relative intensities of L-lines vary with the voltage. In order to give a more general interpretation to the results, the variation of the intensity with voltage was studied. As the voltage is raised, the relative intensity of lines belonging to different excitation potentials undoubtedly approaches a constant ratio, and the value of this ratio can be calculated from the results of measurement at any known voltage if the law of increase is known. It was assumed that in the range studied the intensity could be represented by

$$I = k(V - V_0)^n,$$

where I is the intensity of the line at the voltage V; V_0 is the critical voltage of the line, and k is a constant characteristic of the line. The variation with voltage was first expressed in this form by Webster and Clark.[13] This is in agreement with the procedure of Jönsson, but not in agreement with the theoretical predictions of Bergen Davis[14] which have been confirmed by Wooten,[15] Kettman,[16] and Stumpen[17] at voltages considerably above the critical voltages.

The following table gives the values of n resulting from measurements on the relative intensities of $L\alpha_1$ and $L\beta_{1,5}$ at 31.8, 27.7, and 23.1 kilovolts, respectively. For convenience in tabulation, n is found analytically from pairs of observations on the same line by the formula

[13] Webster and Clark, Phys. Rev. **9**, 571 (1917).
[14] Davis, Phys. Rev. **11**, 433 (1918).
[15] Wooten, Phys. Rev. **13**, 71 (1919).
[16] Kettman, Zeits. f. Physik. **18**, 359 (1923).
[17] Stumpen, Zeits. f. Physik. **36**, 1 (1926).

$$n = \frac{\log I_1 - \log I_2}{\log (V_1 - V_0) - \log (V_2 - V_0)}$$

where I_1 and I_2 are the intensities at two different voltages V_1 and V_2. The critical voltages (in kilovolts) of the thorium L-series are as follows: L_{11}, 20.45; L_{21}, 19.66; L_{22}, 16.29. In view of these results the value of n was taken

TABLE III

Variation in intensity of $L\alpha_1$ and $L\beta_{1,5}$ with voltage.

Observation No.	Voltage (kv)	$\log(V-V_0)$	Intensity (corr.)	log I	Observations used	n calc.
			Observations on $L\alpha_1$			
1	31.8	1.190	13.29	1.123	1, 2	1.96
2	27.7	1.057	7.30	0.863	1, 3	2.07
3	23.1	0.832	2.41	0.382	2, 3	2.14
			Observations on $L\beta_{1,5}$			
4	31.8	1.082	5.99	0.777	4, 5	1.95
5	27.7	0.903	2.68	0.428	4, 6	2.08
6	23.1	0.531	0.43	−0.367	5, 6	2.14

to be 2. There seems to be a slight trend in the values of n, in both $L\alpha_1$ and $L\beta_{1,5}$. The experiments were not pushed far enough to see if this is real or not. The value of n used by Jönsson for tungsten and platinum was 1.7. The correction to be applied to observations at any one voltage is

$$\left(\frac{V - V_0^{\alpha}}{V - V_0^{\lambda}}\right)^2$$

where V_o^{α} is the critical voltage for Th $L\alpha_1$ and V_o^{λ} is the critical voltage for some other line λ.

TABLES OF RESULTS

The results of the individual trials of relative intensities at 31.8 kv and 7.5 m.a. are given in Table IV, and some idea of the experimental errors

TABLE IV

Direct, uncorrected results for the relative intensities of the L-series lines of thorium.

η/l	α_2/α_1	$\beta_{1,5}/\alpha_1$	$\beta_{1,5}/\beta_3$	β_2/β_6	β_1/β_2	β_2/γ_1	γ_1/γ_2	$\gamma_1/\gamma_{3,4}$	β_1/β_7	β_2/η
0.40	0.133	0.380	0.040	0.056	0.695	0.292	0.110	0.344	0.013	0.049
.26	.128	.382	.049	.066	.663	.297	.080	.35	.010	.034
.42	.104	.382	.054		.695	.328	.100			
	.127	.364	.051			.279	.080			
	.106									
	.127									
	.119									
	.112									
0.36	0.12	0.38	0.048	0.061	0.681	0.30	0.092	0.35	0.012	0.042

involved may be gained there. The averaged and corrected results are given in Table V.

TABLE V

Relative intensity of thorium L-series lines.

Line	Observed uncorrected intensity (31.8 kv)	Intensity corrected for absor. (31.8 kv)	Voltage correction	Rel. int. at high voltage
l	3.1	3.6	1.00	3.6
α_2	12	12	1.00	12
α_1	100	100	1.00	100
η	1.1	1.1	1.64	1.8
β_6	1.6	1.4	1.00	1.4
β_2	26	26	1.00	26
β_7	.45	.45	1.00	.45
$\beta_1+\beta_5$	38	38	1.64	62
β_3	1.8	1.8	1.85	3.3
γ_5	0	0	1.64	0
γ_1	7.7	8.5	1.64	14
γ_2	.71	.81	1.85	1.5
$\gamma_3+\gamma_6$	2.7	3.1	1.7	5.3
γ_4	0	0	1.85	0

Two attempts each were made to find indications of the lines γ_4 and γ_5 but no trace of these lines could be found. They must be extremely weak at 31.8 kilovolts.

DISCUSSION OF RESULTS

In comparing these results with theoretical predictions it will be assumed that these theoretical predictions apply to the relative intensities at high voltages, that is, far above the critical excitation voltages. The following predictions of Sommerfeld[18] and of Coster and Goudsmit[19] as to the relative intensities of x-ray doublets and compound doublets can be tested from the observed data.

TABLE VI

Relative intensities of L-doublets.

Lines	Predicted	Observed
$\alpha_1 : \alpha_2 : \beta_1$	100 : 11 : 56	100 ; 12 : 62*
$(\beta_2+\beta_{15}) : \gamma_1$	100 : 50	100 : 53
$l : \eta$	100 : 50	100 : 50

*This value includes $L\beta_5$.

The unfortunate fact that γ_3 lies too near γ_6 to be separated and β_4 could not be separated from β_2 prevents determinations of the relative intensities of the very interesting doublets resulting from electron transitions ending in L_{11}. The results in Table VI show that for the lines representing electron transitions ending in L_{21} and L_{22} the predictions are experimentally

[18] Sommerfeld, Ann. d. Physik. **76**, 284 (1925).

[19] Coster and Goudsmit, Naturwiss. **1**, 11 (1925).

realized. If a rough estimate of the intensity of β_5 is computed (assuming the rules to hold) from half the combined intensity of $\gamma_6+\gamma_3$, and then subtracted from the combined intensity of $\beta_1+\beta_5$ the theoretical ratio of $\alpha_1:\beta_1$ is more nearly approached.

The advent of the new quantum mechanics has made it possible to calculate the relative intensities of lines involving different azimuthal quantum number changes by a new method. Formerly only the correspondence principle was available.[20] This has been carried out by Wentzel,[21] and he has compared his results with those of Jönsson on tungsten. In Table VII this comparison is reproduced and the present results on thorium added.

TABLE VII

Comparison of experimental results on relative intensities of different series with theory. (Wentzel).

Lines	Transitions	Intensity Calc.	Obs. in W (Jönsson)	Obs. in Th
$\alpha_2+\alpha_1+\beta_1$	3_3-2_2	(1.00)	(1.00)	(1.00)
$l+\eta$	3_1-2_2	.02	.03	.03
$\beta_4+\beta_3$*	3_3-2_1	.21	.08	.03
$\beta_2+\gamma_1$	4_3-2_1	.43	.18	.23
$\beta_6+\gamma_5$	4_1-2_2	.01	.01	.008
$\gamma_2+\gamma_3$†	4_3-2_1	.12	.02	.02

* In the experimental work on Th, β_4 could not be separated from β_2. Since the intensity of β_3 was 3.3, by analogy with W, β_4 was taken to be 2.

† γ_3 could not be separated from γ_6 but it is estimated to be about 2 since γ_2 is 1.5.

An interesting fact brought out by Table VII is the weakness of β_4 and β_3 in thorium as compared with tungsten. This is at once apparent from the curve of the β-group (Fig. 2) if one keeps the corresponding curves for tungsten in mind.

Another marked difference between thorium and tungsten is the strength of γ_6 in thorium. Unfortunately the other member of the compound doublet, β_5, is coincident with β_1 so that it cannot be separately measured and compared with β_5 in tungsten.

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May 23, 1927.

[20] F. C. Hoyt, Phil. Mag. **46**, 135 (1923).
[21] Wentzel, Naturwiss, **14**, 621 (1926).

THE SPARK SPECTRUM OF NICKEL (Ni II)

By A. G. Shenstone

Abstract

The analysis of the spark spectrum of nickel shows that the important atomic structures are d^8s and d^8p. The low set of terms comprises $^4F'$, $^2F'$, $^4P'$, $^2P'$, ^2D, ^2G of which $^4F^5{}'$ is lowest. The only expected term from the structure d^8s which has not been found is ^2S. All the intermediate terms (d^8p) have been found with the exception of a ^2P, and a doubtful ^2F and $^2S'$. A higher member of the $^4F'$ $^2F'$ series (d^8, s) has been found and indicates an I.P. of 17.4 volts from d^8s to d^8. The expected lowest term $^2D(d^9)$ has not been found. Terms are inverted with the following exceptions: (1) $a^4G^6{}'$ is higher than $a^4G^5{}'$, (2) $a^4P^3{}'$ is higher than $a^4P^1{}'$, (3) $b^4D^4{}'$ is higher than $b^4D^1{}'$, (4) triad b^2P, D', F is not inverted. Zeeman effects give some irregular g-values, but the g-sum rule is apparently satisfied. The g-sum rule is found to be not confined to terms built on the same ion term.

THE wave-lengths of the spark spectrum of nickel have been measured by various investigators[1] but none of the published lists are sufficiently complete for an extended analysis of the spectral structure. Some time ago Dr. Meggers of the Bureau of Standards made very complete measurements between λ3500 and λ2150 with a view to undertaking such an analysis. Subsequent circumstances, however, made it impossible to start the investigation, and he has been kind enough to allow the author of this paper the use of all of his material. The measurements down to λ2600 were made from plates taken with the Bureau concave grating; and from that point to λ2150 on an Hilger E.1 quartz spectrograph using the copper standards determined by Mitra.[2]

The author has extended the measurements to λ1944 on a similar instrument using the copper spark lines as standards. The frequencies of these lines were determined in the course of the author's analysis of Cu II.[3] The method of calculation was devised by Professor H. N. Russell and determines wave-numbers directly. The wave-lengths below λ2165 given in the table of lines (Table IV) were calculated from the wave-numbers. Three of the strong lines measured by Meggers have been found to be double and have been re-measured. They are noted in Table IV. Measurements were also made on a small Hilger quartz instrument to λ1830. These are, of course, much less accurate. There are, in all, twenty-eight lines which appear reversed in the spark. Most of these, including all the strong reversals, were observed by Meggers as absorption lines in the under-water spark. The line intensities are partly the author's rather rough estimates and partly Meggers'. They have been especially examined in all crucial cases.

[1] H. Kayser, "Handbuch der Spectroscopie," Vol. 6, p. 172.
[2] Mitra, Ann. d. Physique, **19**, 315 (1923).
[3] A. G. Shenstone, Phys. Rev. **29**, 380 (1926).

The structure of the spectrum is deducible from the principles given by Hund.[4] The predicted terms are given in Table I. The electron configurations are denoted by symbols in which small letters (s, p, d, etc.) are use to indicate the k-values of the orbits and indices the number of electrons: Closed groups of electrons are omitted for convenience.

TABLE I

Theoretical and empirical terms in the spectrum of Ni II

Structure	Terms (theoretical)	Terms (empirical)
d^9	^2D	
d^8s	$^4F'$ $^2F'$ $^4P'$ $^2P'$ ^2S ^2D ^2G	a^4F', a^2F', a^4P', a^2P' a^2D a^2G
d^8p	$^4D'$, F, G'. $^2D'$, F, G' $^4S'$, P, D'. $^2S'$, P, D' ^2P ^2P, D', F ^2F, G' H	a^4D', F, G'. a^2D', F, G'. b^4S', P, D' c^2S', P, D' b^2P, D', F c^2F, b^2G', b^2H
d^8, s	$^4F'$, $^2F'$, $^4P'$, $^2P'$ ^2S, ^2D, ^2G.	d^4F', d^2F'

The convention as to the "priming" of the spectral terms is that proposed by Heisenberg.[5] When the atomic structure contains an even number of p (and f) electrons, the terms are called S, P', D, etc.; when the number is odd, S', P, D', etc. Small letters have been used in the term notation merely to differentiate between terms of the same kind. The letters have no other significance.

The empirical terms are contained in Table II, the term values being given with reference to a^4F_5' taken as zero. The expected lowest term ^2D (d^9) has not been found and is discussed below. The lowest term found is a^4F' (d^8s). It is accompanied by a^2F' and combines very strongly with the related triad $a^{4,2}D'$, F, G'. The terms are all inverted and the interval rule holds approximately except for the fact that a^4G_6' is higher than a^4G_5'. This behaviour of the component term of highest j-value in a triad is paralleled in the corresponding terms of Cu II ($^3F_4$) and Ni I ($^3F_4$). The combination $a^4F_5'-a^4G_6'$ is extraordinarily strongly reversed, even appearing as a reversed line in the ordinary arc.

The remaining predicted terms from the low structure d^8s have all been found except ^2S, and are considerably higher than a^4F'. They combine very irregularly with the triad $a^{4,2}D'F\ G'$. Their strong combinations are with their own triads and lie in the same general region of the spectrum as the a^4F' multiplets. The three strongest lines are slightly reversed, namely: $a^2D_3-b^2F_4$, $a^4P_3'-b^4D_4'$, $a^2G_5-b^2H_6$. These lines were not observed by Meggers in the under-water spark.

[4] Hund, Linienspektra und Periodisches System der Elemente, Berlin, 1927, (Julius Springer).

[5] Heisenberg, Zeits. f. Physik. 32, 859 (1925).

TABLE II

Empirical terms in the spectrum of Ni II.

Type	Terms	Intervals		g
a^4F_5'	0.0	936.4		L
a^4F_4'	936.4	785.4		L
a^4F_3'	1721.8	548.3		L
a^4F_2'	2270.1			L
a^2F_4'	5156.2	1445.3		L
a^2F_3'	6601.5			L
a^2D_3	14714.0	688.0		1.46
a^2D_2	15402.0			1.10
a^4P_2'	16394.0	47.8		1.47
a^4P_1'	16441.8	−247.7		L
a^4P_3'	16641.7			1.40
a^2P_2'	20676.5	522.5		L
a^2P_1'	21199.0			L
a^2G_5	24105.3	24.0		L
a^2G_4	24129.3			L
a^4D_4'	43164.0	1180.5		L
a^4D_3'	44344.5			L
a^4G_5'	44971.1	895.5	−131.6	L
a^4G_6'	45102.7			L
a^4D_2'	45241.0	541.0	897.5	L
a^4D_1'	45782.0			L
a^4G_4'	45868.6			L
a^4F_5	46163.2		756.1	L
a^4G_3'	46624.7	860.6		L
a^2G_5'	46905.9			L
a^4F_4	47023.8	657.3	1071.6	L
a^4F_3	47681.1			L
a^2G_4'	47977.5	349.4		L
a^4F_2	48030.5			L
a^2F_4	48686.2	1412.7		L
a^2D_3'	49025.6			L
a^2F_3	50098.9		1285.9	L
a^2D_2'	50311.5			L

Type	Terms	Intervals		g
b^4P_3	58176.8	8.6		1.46
b^4P_2	58185.4	451.2		1.60?
b^4P_1	58636.6			2.36
b^2F_3	59300.1	436.8		.95
b^2F_4	59736.9			L
b^2D_2'	59760.0	581.2		L
b^2P_1	59887.3			1.00
b^2D_3'	60341.2		684.1	L
b^2P_2	60571.4			L
b^4D_3'	62241.1	71.4		L
b^4D_2'	62312.5	41.9		L
b^4D_1'	62354.4	−142.2		L
b^4D_4'	62383.3			L
c^2D_3'	63376.8	604.2		L
c^2D_2'	63981.0			L
c^2P_2	64591.1	917.5		L
c^2P_1	65508.6			?
c^2S_1'	65888.9			?
b^4S_2'	65906.2			L
b^2H_5	66755.5	572.0		L
b^2H_6	67327.5			L
c^2F_3	67495.4?	27.8		?
c^2F_4	67523.2?			L
b^2G_4'	71428.6	101.1		L
b^2G_5'	71529.7			L
d^4F_5'	83404.4	525.4		
d^4F_4'	83929.8	1064.1		
d^4F_3'	84993.9	677.1		
d^4F_2'	85671.0			
d^2F_4'	85132.2	1200.8		
d^2F_3'	86333.0			

The intermediate triads (d^8p) which are intimately connected with a^4P', a^2D and a^2G are complete except for the rather doubtful c^2S', and c^2F terms; but the ^2P which would compose the whole "triad" of the missing low ^2S has not been found. These missing terms are probably somewhat higher.

The high terms d^4F' and d^2F' are undoubtedly the second member of the sequences headed by a^4F' and a^2F'. The similarity with the corresponding

series terms of Cu II, Ni I, Pd I[6] is striking. The over-all separation of the d^4F' is 2266.6 as compared with 2270.1 for a^4F'. Assuming a Rydberg series given by the two terms, the limits of the component series are as follows:

$^4F_5'$	140772	$^3F_4'$
$^4F_4'$	141152	$^3F_3'$
$^4F_3'$	142318	$^3F_2'$
$^4F_2'$	143037	
$^2F_4'$	141284	
$^2F_3'$	142398	

The brackets indicate the pairs of terms which should converge to identical limits in the next higher ion spectrum. It is evident that just as in the other spectra referred to above, there is no indication in the limits calculated from two members of such a convergence. The ionization potential calculated from the $^4F_5'$ is 17.4 volts from d^8s to d^8.

The nature of the terms a^4F', a^2F' and their triads can be deduced simply from a consideration of intensities. That is also true for the large majority of the other terms, but in some cases Zeeman effects have been found necessary to remove any ambiguity. Observations of the Z.E. have, therefore, been made, the patterns measured including the vast majority of the lines of the spectrum. The photographs were taken on a Hilger E.1 quartz spectrograph using Cramer Contrast and Hilger Schumann plates. The magnet was one made for this laboratory in the Ryerson Laboratory in Chicago and produces a field of about 34,000 gauss on continuous operation. The source used was an arc between a plane anode and a knife-edge cathode with a current of about 1.5 amperes. Such a source emits practically the complete spark spectrum. Exposures ranged from a few seconds to twenty minutes. Measurements were made on several plates and averages taken to reduce as far as possible the errors arising from the smallness of the separations. The actual resolving power is greater than 47,000.

Table III contains Zeeman effect of forty-four lines, including all those completely resolved. It seems unnecessary to reproduce the remaining large number of unresolved patterns, since those given are sufficient to fix the only doubtful cases. In the table, where it seems probable that the g-values of the terms agree with Lande's values, they are given as fractions. Where they are given as decimals they are in disagreement with Lande and are not to be considered as possessing great accuracy. Table III has been arranged to show the sequence by which the various g-values were determined.

The Z.E.'s show conclusively that the terms a^4F' a^2F' and their triads have g-values very close to those given by Lande's formula. The case is quite different when we consider a^4P' and a^2D. The two levels a^4P_3' and a^2D_3 should have g's equal to 8/5 and 6/5, whereas they have actually almost equal values. The intensities of their combinations are also irregular. For instance, a^2D_3 combines much more strongly with b^4P_3 than does a^4P_3';

[6] A. G. Shenstone, Phys. Rev. **29**, 380 (1926).

TABLE III

Zeeman effect of forty-four lines in the spectrum of Ni II.

λ	$x-y$	Pattern	g_x	g_y	Remarks
2165.55	$a^4F_5'-a^4F_5$	Obs (0) 1.34	$\frac{4}{3}$	$\frac{4}{3}$	
		Cal (0) 1.33			
2169.10	$a^4F_4'-a^4F_4$	Obs (0) 1.24	$\frac{78}{63}$	$\frac{78}{63}$	
		Cal (0) 1.24			
2175.16	$a^4F_3'-a^4F_3$	Obs (0) 1.00	$\frac{36}{35}$	$\frac{36}{35}$	
		Cal (0) 1.03			
2184.61	$a^4F_2'-a^4F_2$	Obs (0) .39	$\frac{2}{5}$	$\frac{2}{5}$	
		Cal (0) .40			
2158.73	$a^4F_3'-a^4F_2$	Obs (* .94) 0 ** 1.97	$\frac{36}{35}$	$\frac{2}{5}$	Outside components only measured. All present.
		Cal (.31 .94) .08 .71 1.34 1.97			
2201.41	$a^4F_2'-a^4F_3$	Obs (* .90) 0 ** 1.94	$\frac{2}{5}$	$\frac{36}{35}$	
		Cal (.31 .94) .08 .71 1.34 1.97			
2326.44	$a^4F_2'-a^4D_2'$	Obs (.40 1.19) 0 .78 1.60	$\frac{2}{5}$	$\frac{6}{5}$	Used as standard of Z. E.
		Cal (.40 1.20) 0 .80 1.60			
2297.49	$a^4F_2'-a^4D_1'$	Obs (0) .55	$\frac{2}{5}$	0	
		Cal (.2) .2 .6			
2188.05	$a^4F_4'-a^4G_3'$	Obs (** 1.63) *** 2.86	$\frac{78}{63}$	$\frac{4}{7}$	Six resolved σ components and 4 π components on each side.
		Cal (.33 1.00 1.66) .24 .43 .90 1.57 2.24 2.90			
2296.56	$a^2F_4'-a^2F_4$	Obs (0) 1.13	$\frac{8}{7}$	$\frac{8}{7}$	
		Cal (0) 1.14			
2298.28	$a^2F_3'-a^2F_3$	Obs (0) .86	$\frac{6}{7}$	$\frac{6}{7}$	
		Cal (0) .89			
2177.36	$a^4P_1'-b^4D_1'$	Obs (1.33) 1.34	$\frac{8}{3}$	0	
		Cal (1.33) 1.33			
2179.36	$a^4P_1'-b^4D_2'$	Obs (.74) .50 1.96	$\frac{8}{3}$	$\frac{6}{5}$	
		Cal (.73) .47 1.93			
2307.79	$a^4P_1'-b^2D_2'$	Obs (.90) 0 1.80?	$\frac{8}{3}$	$\frac{4}{5}$?	
		Cal (.93) .13 1.73			
2102.84	$a^4P_1'-c^2D_2'$	Obs (.98) 0	$\frac{8}{3}$	$\frac{4}{5}$	
		Cal (.93) .13 1.73			

Where g-values are apparently in agreement with Lande's they are given as fractions; where they are in disagreement they are stated in decimals and are considered as approximate. A * is used to denote the presence of a component which was either too faint to measure or the measurement of which would be inaccurate.

TABLE III. *continued.*

λ	$x-y$	Pattern	g_x	g_y	Remarks
2265.36	$a^4P_1'-b^2P_2$	Obs (.66) $\overline{.61}$ * Cal (.66) $\overline{.66}$ 2.00	$\frac{8}{3}$ $\frac{8}{3}$	$\frac{4}{3}$ $\frac{4}{3}$	
2020.98	$a^4P_1'-b^4S_2$	Obs (?) 1.67 Cal (.33) $\overline{1.67}$ 2.33	$\frac{8}{3}$ $\frac{8}{3}$	2	
2394.84	$a^4P_1'-b^4P_2$	Obs (.55) $\overline{1.03}$ 2.12 Cal (.53) $\overline{1.07}$ 2.13	$\frac{8}{3}$ $\frac{8}{3}$	~1.60 ~1.60	
2369.23	$a^4P_1'-b^4P_1$	Obs (0+) 2.51 Cal (.15) 2.51	$\frac{8}{3}$ $\frac{8}{3}$	~2.36 ~2.36	Used to calculate $g(b^4P_1)$
2366.56	$a^4P_2'-b^4P_1$	Obs (.40) $\overline{1.04}$ 1.97 Cal (.44) $\overline{1.04}$ 1.92	~1.47 ~1.47	~2.36 ~2.36	Gives $g(a^4P_2')$
2312.23	$a^2D_2-b^4P_1$	Obs (.64) $\overline{.46}$ 1.77? Cal (.63) $\overline{.47}$ 1.73	~1.10 ~1.10	~2.36 ~2.36	Gives $g(a^2D_2)$
2177.08	$a^4P_2'-b^4D_2'$	Obs (.39) 1.34 Cal (.14 $\overline{.41}$) 1.06 $\overline{1.34}$ 1.62	~1.47 ~1.47	$\frac{6}{5}$ $\frac{6}{5}$	In agreement with λ2366.
2129.14	$a^2D_2-b^4D_1'$	Obs (.52) * 1.65 Cal (.55) .55 $\overline{1.65}$	~1.10 ~1.10	0 0	In agreement with λ2312.
2247.24	$a^2D_2-b^2P_1$	Obs (0) 1.14 Cal (.05) 1.05 $\overline{1.15}$	~1.10 ~1.10	~1.00 ~1.00	The value of $g(b^2P_1)$ can be obtained only very roughly.
2298.50	$a^4P_2'-b^2P_1$	Obs (.20) * 1.65 Cal (.24) 1.24 $\overline{1.72}$	~1.47 ~1.47	~1.00 ~1.00	
2276.45	$a^2P_2'-c^2P_2$	Obs (0) 1.30 Cal (0) 1.33	$\frac{4}{3}$ $\frac{4}{3}$	$\frac{4}{3}$ $\frac{4}{3}$	
2308.52	$a^2P_2'-c^2D_2'$	Obs (.69) 1.09 Cal (.27 $\overline{.80}$) .53 $\overline{1.07}$ 1.60	$\frac{4}{3}$ $\frac{4}{3}$	$\frac{4}{3}$ $\frac{4}{5}$	Diffuse pattern.
2303.85	$a^2P_1'-c^2P_2$	Obs (.30) 1.10(?) $\overline{1.62}$ Cal (.33) 1.00 $\overline{1.67}$	$\frac{2}{3}$ $\frac{2}{3}$	$\frac{4}{3}$ $\frac{4}{3}$	See λ2276 above.
2236.08	$a^2P_1'-b^4S_2'$	Obs (.70) 1.36 $\overline{2.70}$ Cal (.67) 1.33 $\overline{2.66}$	$\frac{2}{3}$ $\frac{2}{3}$	2 2	See λ2020 above.
2275.70	$a^4P_3'-b^2P_2$	Obs (0) 1.48 Cal (0) 1.45 Blend	~1.40 ~1.40	$\frac{4}{3}$ $\frac{4}{3}$	The determinations of irregular g-values is less accurate in this section since only blend patterns are available.
2319.73	$a^4P_3'-b^2F_4$	Obs (0) .90 Cal (0) .94 Blend	~1.40 ~1.40	$\frac{8}{7}$ $\frac{8}{7}$	
2185.51	$a^4P_3'-b^4D_4'$	Obs (0) 1.40 Cal (0) 1.41 Blend	~1.40 ~1.40	$\frac{10}{7}$ $\frac{10}{7}$	

TABLE III. *continued.*

λ	$x-y$	Pattern	g_x	g_y	Remarks
2287.66	$a^4P_3'-b^2D_3'$	Obs (.23) 1.31 Cal (.40) 1.30 Blend	~1.40	$\frac{6}{5}$	
2179.99	$a^2D_3-b^2P_2$	Obs (0) 1.55 Cal (0) 1.56 Blend	~1.46	$\frac{4}{3}$	
2220.40	$a^2D_3-b^2F_4$	Obs (0) .72 Very diffuse Cal (0) .74 Blend	~1.46	$\frac{8}{7}$	
2054.32	$a^2D_3-c^2D_3'$	Obs (.50) 1.32 Cal (.54) 1.33 Blend	~1.46	$\frac{6}{5}$	
2343.48	$a^4P_3'-b^2F_3$	Obs (1.02) 1.18 Cal (.97) 1.18 Blend	~1.40	~ .95	
2300.10	$a^2D_3-b^4P_3$	Obs (0) 1.46 Cal (0) 1.46	~1.46	~1.46	
2392.58	$a^4P_2'-b^4P_3$	Obs (0) 1.45 Cal (0) 1.46 Blend	~1.47	~1.46	
2405.17	$a^2P_2'-b^4D_3'$	Obs (0) 1.38 Cal (0) 1.38 Blend	$\frac{4}{3}$	$\frac{48}{35}$	
2107.94	$a^2G_5-b^2G_5'$	Obs (0) 1.13 Cal (0) 1.11	$\frac{10}{9}$	$\frac{10}{9}$	
2113.51	$a^2G_4-b^2G_4'$	Obs (0) .88 Cal (0) .89	$\frac{8}{9}$	$\frac{8}{9}$	
2312.91	$a^2G_5-b^2H_6$	Obs (0) 1.03 Cal (0) 1.05 Blend	$\frac{10}{9}$	$\frac{12}{11}$	
2302.48	$a^2G_5-c^2F_4$	Obs (0) 1.02 Cal (0) 1.03 Blend	$\frac{10}{9}$	$\frac{8}{7}$	

but the combinations with b^2F_4 and b^4D_4' have the correct intensity relations and produce reversed lines where they would be expected. It is evidently a case such as occurs in other spectra, of two levels whose identities are more or less fused, and this is in spite of the fact that they arise from the addition of an *s*-electron to different terms of the next higher ion. It should be noted that the *g*-sum is correct within the experimental error, i.e., $1.46+1.40\sim 8/5+6/5$. The case of a^2D_2 and a^4P_2' is similar—the *g*-sum being again shared and the intensity relations being in some cases ambiguous. The balance of evidence is, however, in favor of the identification of terms as given in Table II in spite of the fact that it makes both a^4P' and b^4D' partially re-inverted, the component of largest j in each case being displaced completely over to the high side of the component of smallest j.

TABLE IV

Wave-lengths and classification of lines in spectrum of Ni II.

λ	Auth.	*I*	ν	Designation	λ	Auth.	*I*	ν	Designation
4362.10	Ex	1	22918.3	$a^2G_5-a^4F_4$	2606.40	B	8u	38355.7	$a^2G'_4-d^2F'_3$
4244.80	Ex	1	23551.6	$a^2G_4-a^4F_3$	2605.45	B	3u	38369.6	$a^4G'_3-d^4F'_3$
4192.07	Ex	1	23847.9	$a^2G_4-a^2G'_4$	2601.126	B	8u	38433.4	$a^4G'_5-d^4F'_5$
4067.04	Ex	3	24581.0	$a^2G_5-a^2F_4$	2592.54	B	1	38560.7	$a^2P'_1-b^2D'_2$
4015.50	Ex	1	24896.5	$a^2G_4-a^2D'_3$	2588.31	B	2	38623.7	$a^2P'_2-b^2F_3$
3881.92	Ex	1	25753.2	$b^4P_3-d^4F'_4$	2587.25	B	4	38639.5	$a^2F'_3-a^4D'_2$
3849.54	Ex	2	25969.8	$a^2G_4-a^2F_3$	2584.01	B	8	38688.0	$a^2P'_1-b^2P_1$
3769.45	Ex	5	26521.6	$a^4P'_3-a^4D'_4$	2566.08	B	15u	38958.3	$a^4G'_5-d^4F'_4$
3576.76	Ex	3	27950.3	$a^4P'_2-a^4D'_3$	2565.36	B	2u	38969.2	$a^4F_5-d^2F'_4$?
3513.95	Ex	8	28449.9	$a^2D_3-a^4D'_4$	2560.30	B	10u	39046.2	$a^4G'_3-d^4F'_2$
3471.35	Ex	2	28799.0	$a^4P'_1-a^4D'_2$	2557.88	B	6	39083.2	$a^2P'_2-b^2D'_2$
3465.62	Ex	1	28846.6	$a^4P'_2-a^4D'_2$	2555.13	B	10u	39125.2	$a^4G'_4-d^4F'_3$
3454.16	B	5	28942.3	$a^2D_2-a^4D'_3$	2551.04	B	5	39187.9	$a^2F'_4-a^4D'_3$
3407.30	B	8	29340.4	$a^4P'_1-a^4D'_1$	2549.56	B	8	39210.7	$a^2P'_2-b^2P_1$
3401.76	B	2	29388.2	$a^4P'_2-a^4D'_1$	2547.16	B	3	39247.6	$a^2G_4-c^2D'_3$
3397.82	B	1	29422.1	$a^2P'_2-a^2F_3$	2545.90	B	20	39267.1	$a^2F'_3-a^4G'_4$
3373.98	B	4	29630.2	$a^2D_3-a^4D'_3$	2539.09	B	7	39372.4	$a^2P'_1-b^2P_2$
3350.42	B	5	29838.5	$a^2D_2-a^4D'_2$	2525.42	B	10u	39585.5	$a^4D'_3-d^4F'_4$
3290.69	B	1	30380.1	$a^2D_2-a^4D'_1$	2520.33	B	2	39665.4	$a^2P'_2-b^2D'_3$
3290.54	B	1?	30381.4	$a^4P'_3-a^4F_4$	2514.75	B	6u	39753.5	$a^4D'_2-d^4F'_3$
3274.90	B	3	30526.5	$a^2D_3-a^4D'_2$	2510.87	B	30	39814.8	$a^2F'_4-a^4G'_5$
3208.91	B	1	31154.3	$a^2D_3-a^4G'_4$	2505.84	B	20	39894.8	$a^2P'_2-b^2P_2$
3087.07	B	20	32383.8	$a^4P'_3-a^2D'_3$	2497.80	B	6	40023.2	$a^2F'_3-a^4G'_3$
3063.93	B	2	32628.4	$a^2D_2-a^4F_2$	2484.32	B	10u	40240.3	$a^4D'_4-d^4F'_5$
3032.44	B	2	32967.2	$a^2D_3-a^4F_3$	2473.13	B	15	40422.4	$a^2F'_3-a^4F_4$
2988.05	B	5	33456.9	$a^4P'_3-a^2F_3$	2459.32	B	4U	40649.3	$a^4D'_3-d^4F'_3$
2947.45	B	8	33917.7	$a^4P'_2-a^2D'_2$	2455.51	B	8	40712.4	$a^2F'_4-a^4G'_4$
2942.71	B	1	33972.4	$a^2D_3-a^2F_4$	2437.884	B	20	41006.7	$a^2F'_4-a^4F_5$
2913.59	B	15	34311.9	$a^2D_3-a^2D'_3$	2433.57	B	10	41079.4	$a^2F'_3-a^4F_3$
2882.54	B	1u	34681.5	$a^2D'_2-d^4F'_3$	2432.87	B	1u	41091.2	$a^4D'_2-d^2F'_3$
2881.24	B	2	34697.1	$a^2D_2-a^2F_3$	2431.57	B	8	41113.2	$a^2P'_1-b^4D'_2$
2864.16	B	2U	34904.0	$a^2D'_3-d^4F'_4$	2416.13	B	50R	41375.9	$a^2F'_3-a^2G'_4$
2863.69	B	25	34909.8	$a^2D_2-a^2D'_2$	2413.04	B	8	41428.9	$a^2F'_3-a^4F_2$
2842.41	B	8	35171.1	$a^2G_4-b^2F_3$	2412.25	B	5	41442.5	$a^4F'_3-a^4D'_4$
2836.58	B	1U	35243.4	$a^2F_4-d^4F'_4$	2410.74	B	4	41468.4	$a^2F'_4-a^4G'_3$
2825.23	B	4	35385.0	$a^2D_3-a^2F_3$	2406.89	B	6	41534.7	$a^4P'_3-b^4P_3$
2808.35	B	2	35597.6	$a^2D_3-a^2D'_2$	2406.39	B	5	41543.4	$a^4P'_2-b^4P_2$
2805.67	B	10	35631.6	$a^2G_5-b^2F_4$	2405.17	B	15	41564.4	$a^2P'_2-b^4D'_3$
2775.31	B	6u	36021.4	$a^2D'_2-d^2F'_3$	2398.62	B	2	41677.9	$a^2P'_2-b^4D'_1$
2768.78	B	8u	36106.4	$a^2D'_3-d^2F'_4$	2394.84	B	12	41743.7	$a^4P'_1-b^4P_2$
2760.67	B	2	36212.4	$a^2G_4-b^2D'_3$	2394.50	B	50R	41749.6	$a^2F'_4-a^2G'_5$
2759.02	B	8u	36234.1	$a^2F_3-d^2F'_3$	2392.58	B	10	41783.1	$a^4P'_2-b^4P_3$
2743.01	B	15u	36445.5	$a^2F_4-d^2F'_4$	2392.10	B	6	41791.5	$a^4P'_2-b^4P_2$
2708.78	B	9u	36906.1	$a^4F_4-d^4F'_4$	2387.77	B	25	41867.3	$a^2F'_5-a^4F_4$
2690.62	B	3u	37155.1	$a^2G'_4-d^2F'_4$	2376.01	Ex	1	42074.5	$a^4F'_2-a^4D'_3$
2684.41	B	20u	37241.1	$a^4F_5-d^4F'_5$	2375.43	B	30	42084.8	$a^2F'_3-a^2F_4$
2679.25	B	6u	37312.8	$a^4F_3-d^4F'_3$	2369.23	B	6	42194.9	$a^4P'_1-b^4P_1$
2670.33	B	3	37437.4	$a^2P'_1-b^4P_1$	2367.40	B	20	42227.5	$a^4F'_4-a^4D'_4$
2665.86	B	1	37500.2	$a^2P'_2-b^4P_3$	2366.56	B	10	42242.5	$a^4P'_2-b^4P_1$
2665.25	B	6	37508.8	$a^2P'_2-b^4P_2$	2356.41	B	25	42424.4	$a^2F'_3-a^2D'_3$
2655.90	B	6u	37640.8	$a^4F_5-d^4F'_5$	2350.84	B	8	42525.0	$a^2F'_4-a^4F_3$
2655.46	B	2u	37647.1	$a^2F_4-d^2F'_3$	2345.44	S	15	42622.9	$a^4F'_3-a^4D'_3$
2648.72	B	3	37742.9	$a^2F'_3-a^4D'_3$	2345.26	S	30	42626.1	$a^2G_4-b^2H_5$
2647.04	B	5u	37766.8	$a^4F_5-d^4F'_4$	2343.93	B	4	42650.3	$a^2G_5-b^2H_5$
2632.86	B	5u	37970.2	$a^4F_4-d^4F'_3$	2343.48	B	12	42658.5	$a^4P'_3-b^2F_3$
2631.52	B	2u	37989.5	$a^4F_3-d^4F'_2$	2341.18	B	40	42700.4	$a^2P'_2-c^2D'_3$
2630.29	B	8	38007.3	$a^2F'_4-a^4D_4$	2336.70	S	15	42782.2	$a^2P'_1-c^2D'_2$
2626.57	B	4u	38061.1	$a^4G'_4-d^4F'_4$	2336.59	S	5	42784.2	$a^2D_2-b^4P_2$
2623.10	B	1	38111.5	$a^2G_4-b^4D'_3$	2334.56	B	30	42821.5	$a^2F'_4-a^2G'_4$
2615.20	B	15u	38226.6	$a^2G'_5-d^2F'_4$	2326.44	B	15	42970.9	$a^4F'_2-a^4D'_2$
2611.66	B	3	38278.4	$a^2G_5-b^4D'_4$	2319.73	B	12	43095.2	$a^4P'_3-b^2F_4$
2610.08	B	25u	38301.6	$a^4G'_5-d^4F'_5$	2318.48	B	12	43118.4	$a^4P'_2-b^2D'_2$

TABLE IV. *continued.*

λ	Auth.	I	ν	Designation	λ	Auth.	I	ν	Designation
2316.02	B	80R	43164.2	$a^4F'_5-a^4D'_4$	2175.16	B	25R	45959.2	$a^4F'_3-a^4F_3$
2312.91	B	20	43222.3	$a^2G_5-b^2H_6$	2174.67	B	30R	45969.5	$a^4F'_4-a^2G'_5$
2312.23	S	4	43234.9	$a^2D_2-b^4P'_1$	2169.10	B	30R	46087.6	$a^4F'_4-a^4F_4$
2308.52	B	12	43304.5	$a^2P'_2-c^2D'_2$	2165.55	B	40R	46163.1	$a^4F'_5-a^4F_5$
2307.79	B	8	43318.1	$a^4P'_1-b^2D'_2$	2161.21	B	10	46255.8	$a^4F'_3-a^2G'_4$
2305.24	B	10	43366.1	$a^4P'_2-b^2D'_2$	2158.73	B	8	46308.8	$a^4F'_3-a^4F_2$
				$a^2G_4-c^2F_3$?	2139.08	S	1	46734.2	$a^4P'_3-c^2D_3$
2303.85	B	6	43392.2	$a^2P'_1-c^2P_2$	2138.60	S	10	46744.8	$a^4F'_4-a^4F_3$
2302.98	B	60R	43408.6	$a^4F'_4-a^4D'_3$	2138.08	S	1	46756.1	$a^4F'_2-a^2D'_3$
2302.48	B	10	43418.0	$a^2G_5-c^2F_4$?	2134.28	S	8	46839.4	$a^2D_3-b^4D'_3$
2301.01	B	4	43445.8	$a^4P'_1-b^2P_1$	2131.27	S	3	46905.5	$a^4F'_5-a^2G'_5$
2300.10	B	15	43463.0	$a^2D_3-b^4P_3$	2131.02	S	2	46911.0	$a^2D_2-b^4D'_2$
2299.65	B	8	43471.5	$a^2D_3-b^4P_2$	2130.70	S	0	46918.2	$a^2P'_2-c^2F_3$?
2298.50	B	6	43493.2	$a^4P'_2-b^2P_1$	2129.14	S	3	46952.4	$a^2D_2-b^4D'_1$
2298.28	B	30R	43497.4	$a^2F'_3-a^2F_3$	2128.57	S	12	46964.9	$a^4F'_3-a^2F_4$
2297.49	B	20R	43512.3	$a^4F'_2-a^4D'_1$	2127.77	S	6	46982.6	$a^4P'_2-c^2D'_2$
2297.13	B	30R	43519.2	$a^4F'_3-a^4D'_2$	2125.89	S	4	47024.1	$a^4F'_5-a^4F_4$
2296.56	B	30R	43529.9	$a^2F'_4-a^2F_4$	2125.12	S	8	47041.2	$a^4F'_4-a^2G_4$
2287.66	B	10	43699.3	$a^4P'_3-b^2D'_3$	2113.51	S	12	47299.5	$a^2G_4-b^2G'_4$
2287.10	B	20R	43710.0	$a^2F'_3-a^2D'_2$	2113.29	S	1	47304.6	$a^4F'_3-a^2D'_3$
2278.81	B	30R	43869.0	$a^2F'_4-a^2D'_3$	2112.45	S	1	47323.4	$a^2G_5-b^2G'_4$
2377.31	B	10	43897.9	$a^2D_2-b^2F_3$	2111.75	S	1	47338.9	$a^4P'_3-c^2D'_2$
2276.45	B	5	43914.5	$a^2P'_2-c^2P_2$	2109.01	S	5	47400.5	$a^2G_4-b^2G'_5$
2275.70	B	7	43928.9	$a^4P'_3-b^2P_2$	2107.94	S	18R	47424.5	$a^2G_5-b^2G'_5$
2274.75	B	8	43947.3	$a^4P'_2-b^2D'_3$	2103.39	S	5	47527.2	$a^2D_3-b^4D'_3$
2270.24	B	40R	44034.6	$a^4F'_4-a^4G'_5$	2102.84	S	1	47539.6	$a^4P'_1-c^2D'_2$
2265.36	B	2	44129.4	$a^4P'_1-b^2P_2$	2100.23	S	1	47598.6	$a^2D_3-b^4D'_2$
2264.47	B	30R	44146.8	$a^4F'_3-a^4G'_4$	2097.08	S	12	47670.1	$a^2D_3-b^4D'_4$
2262.90	B	2	44177.4	$a^4P'_2-b^2P_2$	2093.55	S	8	47750.6	$a^4F'_4-a^2F_4$
2256.15	B	8	44309.5	$a^2P'_1-c^2P_1$	2090.14	S	5	47828.4	$a^4F'_2-a^2F_3$
2253.87	B	20R	44354.4	$a^4F'_2-a^4G'_3$	2084.87	S	5	47949.3	$a^4P'_3-c^2P_2$
2253.67	B	6	44358.3	$a^2D_2-b^2D'_2$	2083.76	S	2	47974.8	$a^2D_2-c^2D'_3$
2247.24	B	6	44485.2	$a^2D_2-b^2P_1$	2083.65	S	2	47977.3	$a^4F'_5-a^2G'_4$
2242.14	B	2	44586.4	$a^2D_3-b^2F_3$	2080.84	S	5	48042.1	$a^4F'_2-a^2D'_2$
2236.08	B	2	44707.2	$a^2P'_1-b^4S'_2$	2078.76	S	3	48090.2	$a^4F'_4-a^2D'_3$
2229.85	B	3u	44832.1	$a^2P'_2-c^2P_1$	2076.19	S	1	48149.8	$a^4P'_1-c^2P_2$
2226.34	B	18R	44902.8	$a^4F'_3-a^4G'_3$	2074.13	S	2	48197.6	$a^4P'_2-c^2P_2$
2224.88	B	20R	44932.2	$a^4F'_4-a^4G'_4$	2066.41	S	5	48377.5	$a^4F'_3-a^2F_3$
2224.50	B	2	44939.9	$a^2D_2-b^2D'_3$	2057.81	S	0	48579.7	$a^2D_2-c^2D'_2$
2224.36	B	6	44942.7	$a^2F'_4-a^2F_3$	2057.38	S	2	48589.9	$a^4F'_3-a^2D'_2$
2222.95	B	20R	44971.2	$a^4F'_5-a^4G'_5$	2054.32	S	5	48662.3	$a^2D_3-c^2D'_3$
2220.40	B	10R	45022.9	$a^2D_3-b^2F_4$	2053.30	S	5	48686.4	$a^4F'_5-a^2F_4$
2216.47	B	100R	45102.7	$a^4F'_5-a^4G'_6$	2035.39	S	1	49114.7	$a^4P'_2-c^2P_1$
2213.19	B	7	45169.5	$a^2D_2-b^2P_2$	2033.42	S	3	49162.2	$a^4F'_4-a^2F_3$
2211.09	B	8	45212.4	$a^2P'_2-c^2S'_1$?	2032.30	S	5	49189.4	$a^2D_3-c^2P_2$
2210.38	B	20R	45226.9	$a^4F'_4-a^4F_5$	2029.20	S	10	49264.5	$a^4P'_3-b^4S'_2$
2206.71	B	25R	45302.2	$a^4F'_3-a^4F_4$	2020.98	S	10	49465.0	$a^4P'_1-b^4S'_2$
2201.41	B	20R	45411.2	$a^4F'_2-a^4F_3$	2919.73	S	1	49495.4	$a^4P'_2-c^2S'_1$?
2192.36	S	1	45598.6	$a^4P'_3-b^4D'_3$	2019.03	S	10	49512.6	$a^4P'_2-b^4S'_2$
2190.97	S	2	45627.5	$a^2D_3-b^2D'_3$	2004.27	S	5	49877.2	$a^2D_3-c^2P_2$
2188.91	B	1	45670.5	$a^4P'_3-b^4D'_2$	λ (vac)				
2188.05	B	6	45688.5	$a^4F'_4-a^4G'_3$	1995.74	S	4	50106.7	$a^2D_2-c^2P_1$
2185.51	B	12R	45741.6	$a^4P'_3-b^4D'_4$	1980.73*	S	0	50486.4	$a^2D_2-c^2S'_1$?
2184.61	B	25R	45760.4	$a^4F'_2-a^4F_2$	1980.05	S	4	50503.8	$a^2D_2-b^4S'_2$
2180.46	B	10	45847.5	$a^4P'_2-b^4D'_3$	1965.37	S	8	50881.0	$a^4P'_3-c^2F_4$?
2179.99	B	3	45857.4	$a^2D_3-b^2P_2$	1956.97	S	6	51099.3	$a^4P'_2-c^2F_3$?
2179.46	S	3	45868.5	$a^4F'_5-a^4G'_4$	1953.43	S	8	51192.0	$a^2D_3-b^4S'_2$
2179.36	S	6	45870.7	$a^4P'_1-b^4D'_2$	1893.52*	S	1	52811.7	$a^2D_3-c^2F_4$?
2177.36	B	6	45912.7	$a^4P'_1-b^4D'_1$	1881.14*	S	4	53159.2	$a^2F'_3-b^2D'_2$
2177.08	B	6	45918.7	$a^4P'_2-b^4D'_2$	1812.07*	Bl.	4	55185.4	$a^2F'_4-b^2D'_3$

B. Bureau of Standards.
Ex. Exner and Hascheck. (Kayser. "Handbuch der Spectroscopie." Vol. VI. p. 172)
S. Author.
* Measured on low dispersion.
Bl. Bloch. "Jour. d. Physique" Vol. VI., 105, 1925.

Amongst the intermediate set of terms there are further cases of the sharing of the g-sum, i.e., b^4P_3 and b^2F_3; b^4P_1 and b^2P_1. The term b^4P_2 has certainly $g<26/15$, the theoretical value, and would form a real exception unless b^2D_2' is also irregular, which is quite possible. The terms a^2P' and a^2G have Lande g's, as would be expected from their isolation from other terms. A consideration of all the cases of the sharing of the g-sum in Ni II, Cu II and Cu I indicate that the only necessities are identical j's and electron configurations. It is not essential that the terms should be members of series converging to the same ion term or that they should be particularly close. For instance in Ni II a^2D_3 and a^4P_3' are separated by nearly 2000 cm^{-1} and are built on ion terms ^1D and $^3P'$.

The division of the intermediate doublet terms into particular triads cannot be carried out with certainty, but it is reasonable to group them in the order of magnitude; i.e., b^2P, D', F with a^2D; c^2S', P, D' with a^2P; b^2G', b^2H and c^2F with a^2G. The arrangement is unsatisfactory in that the combinations of b^2D_3' with a^2D are much too faint; and that the grouping is rather closer than would be expected. The terms c^2S' and c^2F are both doubtful.

It is mentioned above that the lowest term of the spectrum would be expected to be a $^2D(d^9)$. The approximate position of this term can be fixed from the terms of the arc spectrum. In the arc, the low structures d^8s^2 and d^9s have practically the same energy. The removal of an s-electron from d^8s^2 (to d^8s), by analogy with other spectra, should require about 5000 to 10,000 cm^{-1} more "energy" than the removal from d^9s (to d^9).[7] But these are the two spark structures concerned in the difference $^2D(d^9)-a^4F'(d^8s)$. The ^2D should, therefore, lie about 5000 to 10,000 cm^{-1} lower than a^4F'. Since ^2D should be the lowest term, its combinations with d^8p might be expected to be very intense. A thorough search through the wave-length lists of L. & E. Bloch[8] has been made unsuccessfully. Some possible sets of lines have been found but nothing which can be accepted with any certainty at all. This point is, therefore, left open. A similar state of affairs exists in the case of Cu II where the lowest term $^1S(d^{10})$ has not been found in spite of a thorough search of the proper region using excellent wave-lengths measured by R. J. Lang at the University of Alberta, Canada. The apparent absence, or at any rate low intensity of the expected combinations in these two cases, requires explanation.

This analysis of Ni II accounts for the vast majority of the strong lines of the spectrum. There are still numerous diffuse lines unidentified but they are undoubtedly due to higher terms, which normally produce hazy lines.

Dr. H. N. Russell of the Department of Astronomy in this University has taken great interest in the progress of this analysis, and has been of the greatest assistence both practically and theoretically. The author thanks him very sincerely. Thanks are also due to Mr. J. J. Livingood for

[7] Laporte, Zeits. f. Physik. **39**, 127 (1926).

[8] L. & E. Bloch, Jour. d. Physique, **6**, 105 (1925).

his very considerable assistance in the experimental and computational work. As mentioned above, the analysis was made possible through the courtesy of Dr. Meggers of the Bureau of Standards in allowing the author full use of all of his observational material.

PALMER PHYSICAL LABORATORY,
PRINCETON UNIVERSITY.
June 16, 1927.

DOUBLET SEPARATION AND FINE STRUCTURE OF THE BALMER LINES OF HYDROGEN[1]

By Norton A. Kent, Lucien B. Taylor and Hazel Pearson

Abstract

Using two optical trains, (1) two crossed Lummer plates, the larger of resolving power of about 670,000, and (2) an echelon of resolving power of about 660,000, the writers have determined the wave-length difference between the two well known components λ' and λ'' ($\lambda' > \lambda''$) of Hα, Hβ and Hγ as 0.1370, 0.0791 and 0.0666A respectively. These values are in good agreement with those obtained by Houston with an interferometer, which latter are in our estimation the most reliable thus far obtained.

Further, microphotometer curves of enlargements of the original Lummer plate negatives reveal another component in λ' unresolved but unquestionably present, in Hα, Hβ and Hγ. Hansen noticed assymmetries here in Hα and Hβ. There are also indications of other components in λ''. The *magnitudes* of these components agree well with the theoretical magnitudes given by the new quantum mechanics with the spinning electron.

Object of the Investigation

THE object of this study was two-fold: (I) to measure the doublet separation of Hα, Hβ and Hγ, and (II) to search for further structure, using large instruments, the dispersion of the large Lummer plate and the resolving powers of this plate and the echelon being in general about twice that of instruments used by others.

The importance of the investigation lies in its bearing upon the various theories of atomic structure. It was undertaken in an attempt to verify the old quantum theory, the new quantum mechanics, with the spinning electron of Goudsmit and Uhlenbeck[2] not having been advanced at that time.

Historical Survey

Critical analyses of the errors which may enter into the determination of the difference in wave-length of closely adjacent lines, particularly the Balmer series doublets, with the addition, in some cases, of new data, have been made by Oldenberg,[3] Lau,[4] Janicki[5] and others. There may enter:

(1) An instrumental error—the "shrinking effect," which occurs when the resolving power of the spectroscope is just sufficient to separate the lines. The curves then overlap and the intensity maxima approach each other.

[1] Preliminary reports of this work have appeared in Nature **119**, 163 (1927) and Phys. Rev. **29**, 748 (1927).

[2] S. Goudsmit and G. E. Uhlenbeck, Physica **6**, 273 (1926).

[3] Oldenberg, Ann. d. Physik. **67**, 253 (1922).

[4] Lau, Phys. Zeits. **25**, 60 (1924).

[5] Janicki, Ann. d. Physik. **76**, 561 (1925).

(2) A visual error, due to the fact that the eye locates the most intense blackening near the edge of the image which possesses the steepest intensity gradient.

(3) A photographic error—the maximum blackening of the plate appearing on the outer edges of narrow doublets, that is where the developer possesses the greater concentration.

Janicki measured by machine the published reproductions of the photographic plates taken by Schrum,[6] with a Lummer plate, and thus eliminated the visual error. Smaller values of $\Delta\lambda$ thus resulted. The two other errors (1) and (3) are least in the lower orders of a Lummer plate pattern as the images here are of less intensity and lie further apart.

Van Cittert[7] discusses mathematically the determination of $\Delta\lambda$ with a Lummer plate, criticizes this instrument severely and, while citing other sources of error, such as (a) the mist of diffused light and (b) the continuous background (these of course being possible with other instruments as well) emphasizes especially: (a) The effect of changes in the coefficient of reflection within the plate at its surface, as one passes from the central region of the pattern. $\Delta\lambda$ is thus decreased but even in the lowest orders the error is small. (b) A change in the image which is formed because the Lummer plate modifies the intensity distribution and produces in the lower and weaker orders an approach of the components of a doublet.

Hansen,[8] giving results obtained with several Lummer plates, discusses in an extensive paper the intensity assymmetries of the hydrogen doublets, tabulates corrections to be made for the shrinking effect as a function of the "saddle height" between the maxima of the curves, cites the effect of decrease of the reflection coefficient as one passes from lower to higher orders, this causing a decrease in $\Delta\lambda$; and cites also a decrease in the sharpness of the interference as causing an increase in the relative saddle height. He further discusses the size of the illuminating slit of the registering photometer and the effect of the inequality of the curves traced by the machine, causing an increase in $\Delta\lambda$ as one passes to higher orders. These and other errors we summarize in Table I, together with methods of elimination.

The variations in the values obtained in previous investigations, some of the most recent of which are listed in Table II, are not at all surprising in view of these numerous errors which may enter, especially with the use of the Lummer plate and echelon. The influence of these errors is well illustrated in the values of $\Delta\lambda$ given in Tables IV to VII.

As to fine structure: Considerable attention has been given to the influence of the Stark effect in bringing up components which, on the old quantum theory, were ruled out by the principle of selection. Hansen feels that the presence of another component in λ', the shorter wave-length component of the doublet, has been proven by him by an observed assymmetry; and that λ'' is possibly double is shown by the variation in the relative intensities of the components of the main doublet with a variation of pressure.

[6] Schrum, Proc. Roy. Soc. London **A105**, 259 (1924).
[7] Van Cittert, Ann. d. Physik. **77**, 372 (1925).
[8] Hansen, Ann. d. Physik. **78**, 558 (1925).

TABLE I

Errors which may enter into the determination of the difference in wave-lengths of closely adjacent lines.

Nature of Error	Advancing to higher orders $\Delta\lambda$ is:—	Lummer Plate		Echelon		Fabry-Perot Interferometer	
		Magnitude	To eliminate	Magnitude	To eliminate	Magnitude	To eliminate
I. Instrumental							
a. shrinking	decreased	variable	use lowest orders	variable	use "faint" plates	variable	adjust mirror distance[4]
b. reflection coefficient[1]	decreased	very small	use lowest orders	negligible		negligible[3]	
c. intensity distribution[2]	increased	large in lowest orders	use higher orders	very large	Use microphotometer and correct errors. See IV b, below	negligible	
II. Visual	increased	This error may be large in all these instruments, if dense plates be used; but it may be avoided by using a microphotometer.					
III. Photographic							
a. Developer	increased	Error *a* is probably small if not negligible and may be avoided by long development with weak developer and sufficient rocking of the plate.					
b. "Mist"[5]		Errors *b* and *c* are variable in magnitude and may be eliminated by excluding extraneous light and exposing and developing properly.					
c. Continuous background							
IV. Microphotometer							
a. Slit width		A slit sufficiently narrow to resolve the lines is necessary. If the slit be too narrow the plate grain may vitiate the curves. To remedy this, increase the slit length. This must not, however, be pushed too far with echelon, and especially interferometer, images, for they are curved. With the interferometer if a long slit be necessary the outer orders may be used as their radii of curvature are greater.					
b. Inequality of heights of curve		Error *b* is not strictly a microphotometer error but arises from I, *c*. It is variable in magnitude and is largest in the lowest orders of the Lummer plate pattern. An approximate correction may be made for it by measuring distances from the points of tangency of curves joining the peaks of the components.[6]					

[1] The decrease of the value of the reflection coefficient with increasing angle of incidence within, and against the surface of, the plate causes (1) a loss of light which decreases as we proceed toward higher orders, and (2) a decrease of the sharpness of the interference.

[2] This error enters strongly in the lowest orders and is especially great in a plate of large dispersion.

[3] If the interferometer be adjusted properly this error does not exist: the rings are of equal intensity although the dispersion decreases from the center outward.

[4] Adjust the distance between the mirrors so that, with a doublet such as Hα, the successive images of one component lie quite accurately between those of the other.

[5] See Van Cittert, Ann. d. Physik **77**, 4, Nt. 12.

[6] See Hansen, Ann. d. Physik **78**, 6, Nt. 22, Fig. 7 of p. 571.

TABLE II

Certain recent determinations of $\Delta\lambda$ in Angstroms.

	McLennan and Lowe[9] 1912	Gehrcke and Lau[10] 1922	Geddes[11] 1922	Oldenberg[3] 1922	Schrum[6] 1924	Schrum and Janicki[12] 1925	Hansen[8] 1925	Janicki and Lau[13] 1925	Houston[14] 1926
H_α	.154	.126	.146	.140	.141	.130	.135–38	.132	.1358
$H\beta$	.085	.071	.078		.085	.076	.075	.072	.0782
$H\gamma$	.062	.056			.070	.060	.062	.059	.0665

Janicki and Lau remeasured with a microphotometer certain of their plates and obtained results which pointed to the presence of five components, which structure would confirm the old quantum theory with a modified selection principle.

[9] McLennan and Lowe, Proc. Roy. Soc. London **A100**, 217 (1921).

[10] Gehercke and Lau, Ann. d. Physik. **67**, 388 (1922).

[11] Geddes, Proc. Roy. Soc. Edin. **43, 1**, 37 (1922).

[12] Schrum and Janicki, Ann. d. Physik. **76**, 561 (1925).

[13] Janicki and Lau, Zeits. f. Physik. **35**, 1 (1925).

[14] Houston, Astrophys. J. **64**, 81 (1926).

Apparatus and Experimental Procedure

The spectroscopic systems are sketched in Fig. 1. The crossed Lummer plate system *A* consisted of (a) a Hilger constant deviation spectroscope fitted to hold the small Lummer plate, L_1, dispersing vertically and (b) a second spectroscope for the large plate, L_2, dispersing horizontally. The echelon system *B* contained the echelon[15] and constant deviation prism in

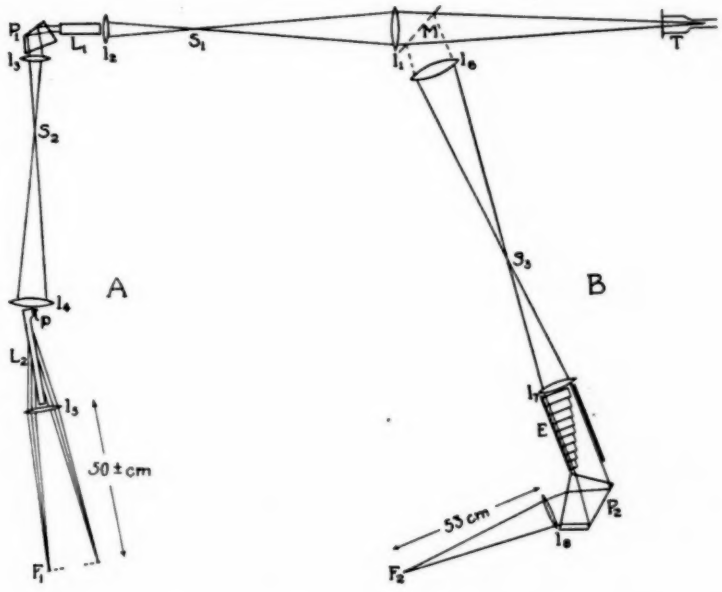


Fig. 1. Arrangement of spectroscopes. *T*, vacuum tube; *M*, plane mirror; $l_1 \cdots l_8$, lenses; L_1, L_2, small and large Lummer plates; P_1, P_2, prisms; F_1, F_2, focal planes of l_5 and l_8; S_1, S_2, S_3, slits; *p*, rotation point of large plate.

tandem in one instrument. The light for *B* was taken off by a mirror, *M*, which caught the light that would otherwise pass through the lower half of lens l_1, and be thrown away at the front end of plate L_1. The constants of the Lummer plates are shown in Table III.

Table III

Constants of the Lummer plates.

	Small plate	Large plate
Thickness	0.4827 cm	0.9963 cm
Length	13.1	30.0
Width	1.45	3.98

Line	λ(A)	Small Plate μ	Small Plate dμ/dλ(A^{-1})	Small Plate Δλ$_m$(A)	Large Plate μ	Large Plate dμ/dλ(A^{-1})	Large Plate Δλ$_m$(A)
H_α	6563	1.50746	− 315.436	−0.38606	1.57187	− 513.607	−0.17204
$H\beta$	4861	1.51560	− 725.535	−0.20645	1.58581	−1301.47	−0.09038
$H\gamma$	4341	1.52025	−1023.67	−0.16210	1.59417	−1941.01	−0.07006

[15] Described in Prod. Amer. Acad. Arts and Sciences 57, 1 (1921).

The maximum theoretical resolving powers for Hα are, approximately, for the small plate, 300,000; for the large plate, 670,000; and for the echelon 660,000.

Lens l_5 was a compound monochromat, made by Bausch and Lomb, the field being flat to within a small fraction of a mm over a central region 5 cm in diameter.

The source was a Pyrex glass tube of the Wood[16] form (see Fig. 2). The capillary could be cooled by running water or by liquid air.

The discharge was obtained by a transformer kindly lent us by Professor Pierce of the Cruft Laboratory at Harvard. The current in the secondary circuit was maintained constant during an exposure and the pressure was held at such a value that the positive column striations were clearly marked.

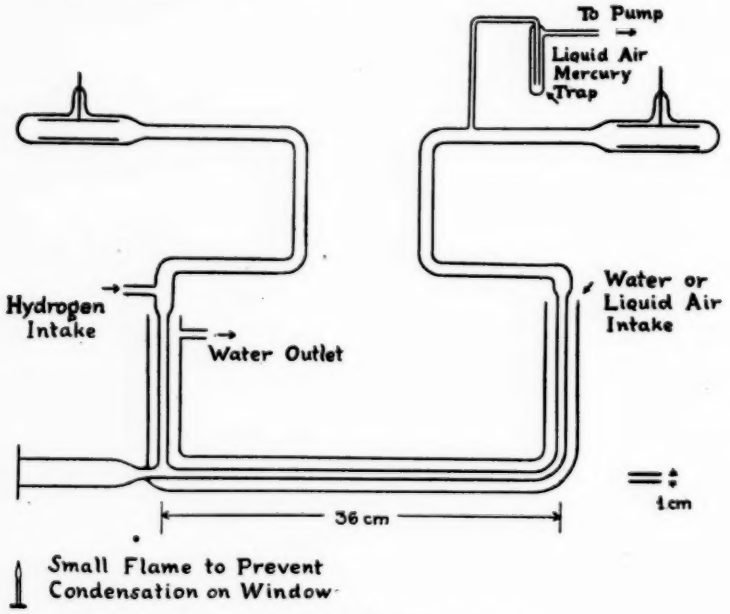


Fig. 2. Vacuum tube used as source.

Visual observation showed that the width of the lines decreased with current density. We therefore used generally but about 25 ma./cm². During exposures the temperature seldom changed more than 0.2°C and usually much less. The hydrogen was led into a reservoir containing water and thence passed to the discharge tube through a long capillary.

With the conditions under which we worked the preliminary formation of an ice film within the discharge tube, as suggested by Schrum,[6] was found unnecessary. The secondary spectrum could be almost eliminated, even at liquid air temperature, by obtaining proper conditions of pressure and amount of water vapor.

An attempt was made to increase the electron emission in the discharge tube by means of tungsten filaments. Three of these, kindly presented to

[16] Wood, Proc. Roy. Soc. London **A97**, 455 (1920).

us by Dr. Coolidge of the General Electric Co., were mounted, one each, near the two terminals and one near the capillary of the tube. With the conditions under which we were obliged to work, notably with much water vapor present, no enhancement of the Balmer series was observed, although the three filaments were used singly, in pairs, and all at once. They were therefore removed.

The dispersion of our 30 cm Lummer plate was such that the image of the nth order of the longer wave-length component of each of the three doublets was almost coincident with the $(n+1)$th order of the component of shorter wave-length: hence the use of the smaller plate to separate these components. The resulting cross pattern had disadvantages from the standpoint of the quantitative evaluation of the wave-length differences

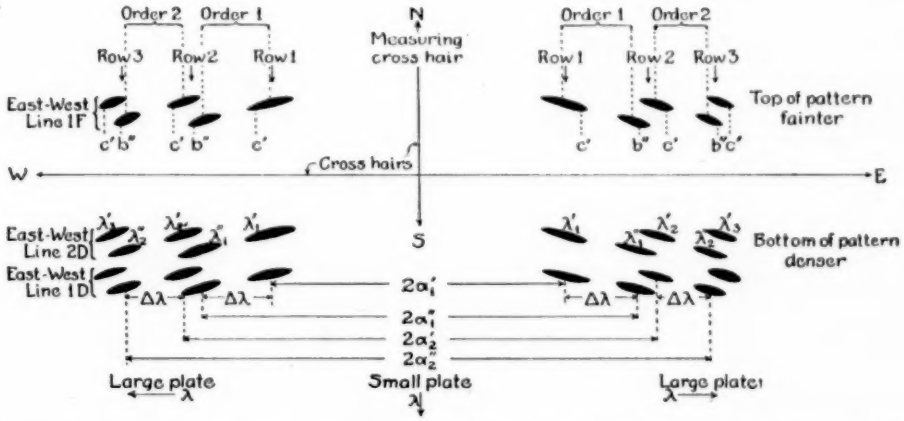


Fig. 3. Crossed Lummer plate pattern of Hα. Line of motion of plate in being measured is East-West. E-W line 1F contains the faintest orders of λ′ and λ″ given by the small Lummer plate; E-W line 1D, the densest. Rows "1" (on left and right sides of the pattern) contain only λ′, the shorter wave-length component of the doublet. Rows "2" contain the second orders of λ′ and the first of λ″. The theoretical positions of the components c' of λ′ and b'' of λ″ are indicated on the E-W line 1F above the letters c' and b''.

between the components, for the pattern is composed of slanting lines as shown in Plate I and schematically in Fig. 3; but the combination of the two plates increased the chances of observing the presence of other than the well-known pair of components.

The equation used in determining Δλ, or the difference in wave-length between the two components of these doublets, as given by the Lummer plate system, was that of McLennan and McLeod[17] namely

$$\Delta\lambda = \frac{\alpha_s^2 - \alpha_n^2}{\alpha_{n+1}^2 - \alpha_n^2} \cdot \Delta\lambda_m$$

where n is the number of the order as seen on the photographic plate; α_n, α_s are the distances of the images of the nth order of lines of wave-length λ,

[17] McLennan and McLeod, Proc. Roy. Soc. London **A90**, 246 (1914).

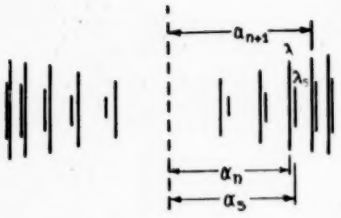


Fig. 4. Single Lummer plate pattern.

and λ_0 (see Fig. 4) from the center of the pattern; $\Delta\lambda_m$ is that change in wave-length which would cause the image of the nth order of a pattern given by a wave-length of $(\lambda+\Delta\lambda)$ to coincide with the image of the $(n+1)$th order of the pattern for λ.

$\Delta\lambda_m$ may be calculated from the constants of the Lummer plate and the various values of α may be measured on the original negatives or machine tracings made therefrom. Although approximations are made in its development, this formula is accurate except for the very highest orders. $\Delta\lambda$ calculated from the 20th order is affected by only a few parts in the fourth decimal place of Angstroms.

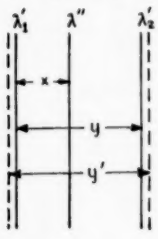


Fig. 5. Echelon pattern.

In obtaining $\Delta\lambda$ with the echelon, the axis of the instrument was set as nearly parallel to the incident light as was possible, but so that at least one component of the doublet was in double order condition, e.g., λ_1' and λ_2' as in Fig. 5. From the known constants of the instrument the distance, Δ_o, between these two images, was calculated. The values of Δ_o in Angstroms, after small negative corrections for prism dispersion are: for Hα, 0.3055; for Hβ, 0.1568; and for Hγ, 0.1214. Then $\Delta\lambda = x\Delta_o/y$.

This process may be criticized on the ground that, as λ_1' and λ_2' are not extremely narrow and also lie near the outer regions of the intensity curve of the instrument, the measured distance, y, would be too small. λ'', however, lies so nearly midway between λ_1' and λ_2' that both x and y would suffer nearly equal percentage changes, and thus $\Delta\lambda$ would remain unchanged. This reasoning holds for Hα, Hβ, and Hγ. It relieves us of the necessity of determining the true distance, y', at which narrow lines would lie.

Methods of Measurement

The plates obtained with the crossed Lummer plate system, indicated by the letter L were measured:

(a) Visually, by a Gaertner comparator. Settings were made—on the center of the slanting images in any given East-West line—by the North-South cross hair—set, for instance, as indicated in Fig. 3, on "Line 1 D."

(b) Mechanically by the Moll recording microphotometer of the Harvard Observatory, kindly put at our disposal by its Director, Professor Shapley. To obtain these curves, the plate was moved past the luminous rectangle R of Fig. 6 so that there were exposed on the first run only the images of the shorter wave-length component, e.g., λ_1', λ_2', λ_3', etc. lying aslant on any one horizontal line of Fig. 3. The plate case was then moved up in its recess so as to unmask the corresponding East-West line of the longer wave-length images λ_1'', λ_2'', λ_3'', etc., and a second run was made. As the vertical height of the photometer slit was but 0.2 mm, the intensity of illumination was low.

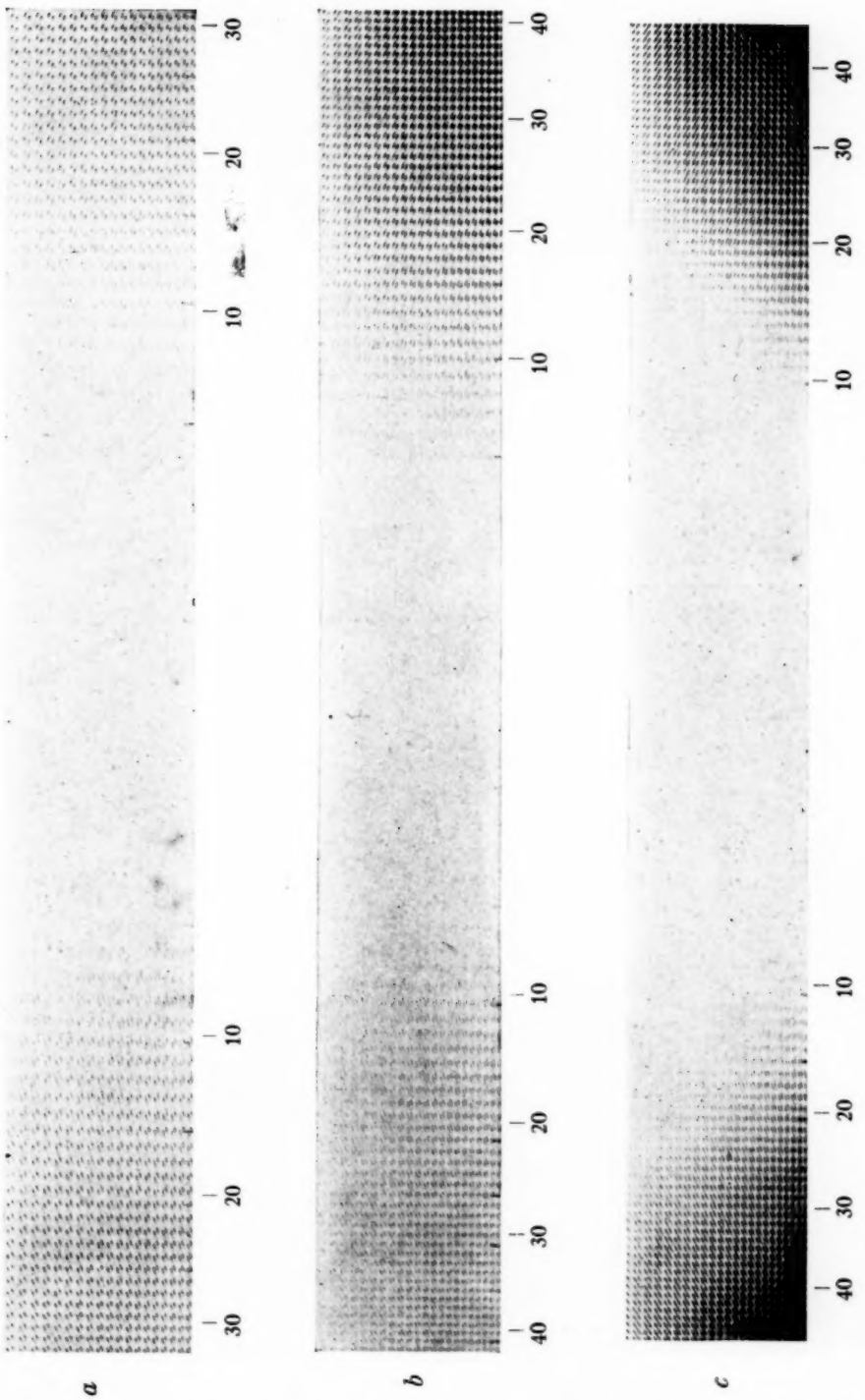


Plate I. Pattern *a* is Plate 4 for Hα; *b* is plate 10 for Hβ; *c* is plate 25 for Hγ. The magnification is 4.2 fold. See Fig. 3 and Plate II as aids in studying the pattern. The numbers refer to rows.

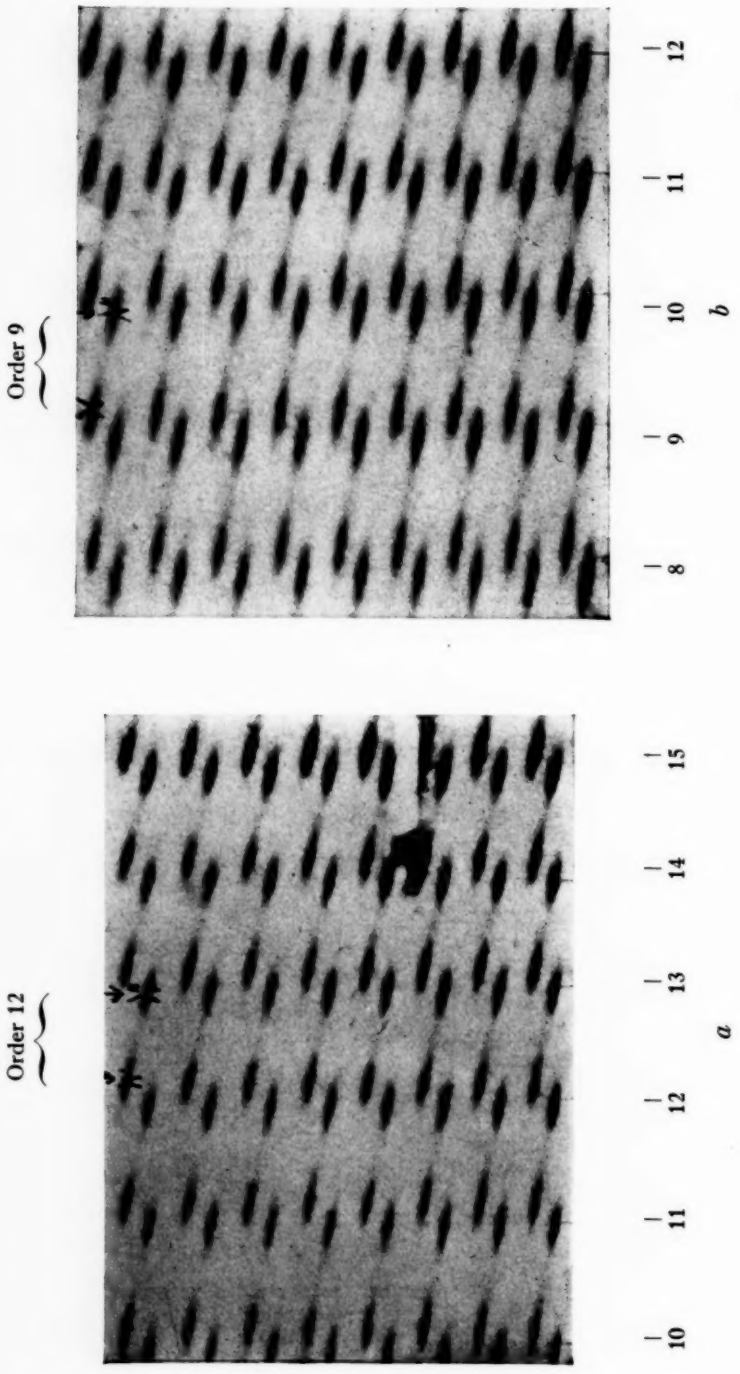


Plate II. Pattern *a* is plate *L2* for Hα, magnification 32 fold; pattern *b* is plate *L7* for Hα, magnification 28 fold. Observe the persistent assymetry toward the right in λ'.

The plates obtained with the echelon, indicated by the letter *E*, were measured: (a) Visually by the Gaertner comparator. (b) Mechanically, by the Moll microphotometer and later, through the kindness of Dr. Adams and Dr. Pettit of the Mt. Wilson Observatory by the microphotometer of that laboratory.

RESULTS

I. *Doublet Separation.* The values of $\Delta\lambda$ obtained from the patterns given by the crossed Lummer plates are shown in Tables IV to VI. There appear therein none obtained from the microphotometer curves. The latter values are almost without exception from 6 to 11 percent higher than the corresponding values determined visually. The reason for this is as follows:

$\Delta\lambda$ depends upon the East and West separation of the density maxima of λ' and λ'' (see Fig. 6). The background of the plate is more dense in regions *D* than *d* and, as the plate passes along so that the small rectangle of

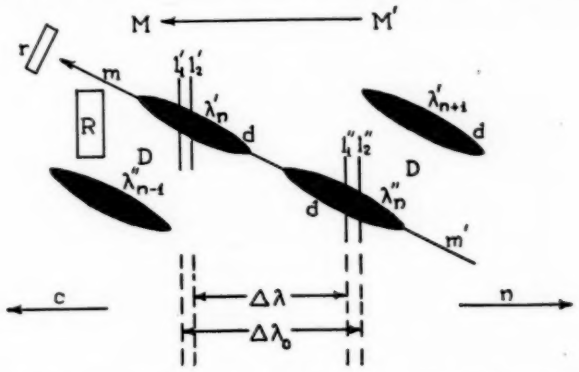


Fig. 6. To illustrate method of measuring plates with the microphotometer. *R*, *r*, luminous rectangles; *M*, *M'* and *m*, *m'*, direction of motion of the plate past the luminous rectangles *R*, *r* in the study of the doublet separation and fine structure, respectively; $\Delta\lambda$, true doublet separation; $\Delta\lambda_0$ separation recorded by the microphotometer; *c*, *n*, direction of center of pattern and higher orders, respectively; *D*, regions of background of plate denser than regions *d*.

light falls upon the images of λ', the galvanometer registers a maximum density for them too near the center of the pattern, i.e., at l_1' instead of l_2', while on the following run, when the plate is moved up and the λ'' images are unmasked, the density maxima are registered as at l_2'' instead of l_1''.

Thus the λ' maxima are shoved *toward*, and the λ'' maxima *away from* the center of the pattern. Both these displacements increase $\Delta\lambda$ and the error increases with the density of the images. This error affects less the *visual values* of $\Delta\lambda$ because the eye does not integrate the density over a rectangular region, as does the machine, but locates the maximum blackening along the slanting line of the image. These curves then are of little value in the quantitative determination of $\Delta\lambda$. We are limited, therefore, to the visual measurements.

Of the errors summarized in Table I, the shrinking effect enters in only one plate *L*21 for Hγ for the images generally used, those of the orders below

the 20th, are well separated. The reflection coefficient error is negligible. The intensity distribution error is prominent. The images of the shorter wave-length component lie so much nearer the center of the pattern than those of the longer that their maxima are displaced outward more and $\Delta\lambda$ is thereby decreased. It will be noticed, in Tables IV and V, that in all cases the low orders give low values. It is here, however, that the microphotometer curves do aid us, for from them we can determine how many of the low orders should be rejected because of too great a change in intensity from one order to the next. We thus use only those values which are given in bold faced type. Further, in the dense plate $L15$ for Hβ (Table V) there

TABLE IV

	Hα						Hβ			
Plate No.	L4	L8	L2	L3	L7	L30	L10	L13	L14	L21
Current (ma/cm²)	24	24	24	24	24	13	24	24	24	24
Exposure (min.)	20	22	25	45	55	70	30	15	19	30
Character	Faint	Faint	Medium	Medium	Medium	Medium	Faint	Medium	Medium	Medium
E-W line No.	10	10	10	10	10	10	12D	12D	12D	11D
Order No. 3					.131					
4				.132	.133				.077	.078
5		.133	.132	.132	.134			.075	.078	.079
6		.135	.134	.134	.135	.133		.077	.080	.079
7	.134	.136	.134	.135	.137	.135		.076	.078	.080
8	.137	.136	.135	.134	.135	.138	.076	.075	.079	.081
9	.137	.138	(.129)	.136	.136	.140	.077	.079	.081	.081
10	.136	.137	.137	.136	.138	.140	.077	.079	.081	.081
11	.136		.135	.137	.138	.139	(.073)	.080	.079	.081
12	.136		.137	.138		.140	.077		.080	.081
13	.135		.137	.137		.140	.078		.081	.081
14	.136		.134	(.130)		.139	.076		.080	.080
15	.140		.140			.139	.078		.079	.081
16	.136		.139			.137			.079	
17	.139					.138			.078	
18	.140					.138			.080	
19	.139					.140			.082	
20	.138					.143			.080	
21	.143					.141			.079	
22	.137					.139			.080	
23						.138			.081	
24						.138			.082	
25						.136			.081	
26						(.117)				
27						.140				
28						.138				
29						.140				
30						.140				
Mean $\Delta\lambda$	$.137_7$	$.137_8$	$.137_8$	$.136_1$	$.136_4$	$.139_1$	$.077_2$	$.077_7$	$.080_8$	$.080_9$
Weighted mean of means				$.137_1$					$.079_4$	

exists a small progressive increase of $\Delta\lambda$ with increase in density of the images whether we advance along any of the arrows a to f. Precisely the same effect enters in a dense Hα plate, $L25$ (not shown). This is probably a visual error, much resembling that which vitiated the results of the microphotometer tracings.[18] In $L21$ for Hγ, a very dense plate, the shrinking effect also enters and prevails. We thus rejected $L25$ and $L15$ entire and saved only the central values in $L21$ as it seemed probable that the two errors here offset each other.

By methods similar to those used in Table IV we obtain for Hγ mean values of $\Delta\lambda$ (plates $L18$, $L19$, and $L21$) 0.064_8, 0.065_3 and 0.067_3, respectively, which yield a weighted mean of means of 0.066_4. The weighted mean

[18] The increase cannot be due to the coming out of component c'' of Fig. 7 which would displace the center of gravity of the λ'' system at the most but 0.001A.

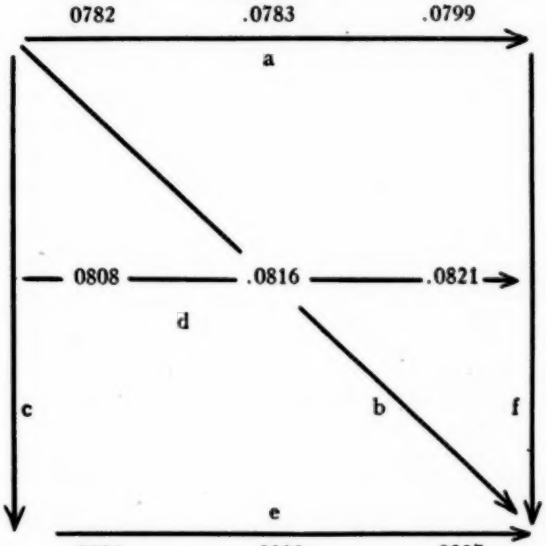
is determined in all cases by giving each mean a weight equal to the number of orders used. In Table IV *L*30 gives, at the very low current density of 13 ma/cm², a value for $\Delta\lambda$ of 0.139_1. We shall return to this point later.

The doublet separations as determined by the echelon are given in Tables VI and VII. All the plates taken which were suitable for visual measurement were used (the densest plates being rejected). From the best of these plates microphotometer tracings were made.

TABLE V

Plate No. L 15 for Hβ

Line No. Order No.		2F and 3F Faint	13D and 12D Medium	3D and 2D Dense
4	Faint	0782	.0783	.0799
14	Medium	0808	.0816	.0821
24	Dense	0824	.0823	.0827



The chief errors entering with the echelon are: First, the shrinking effect. This could not be avoided in the visual measurements, but in the case of the microphotometer curves the saddle heights were obtained and corrections made using Hansen's table for *symmetrical* doublets. In using these we assume symmetry which is not strictly the case; but the error must be small. Second, the visual error. This is present in all the measurements but was avoided as much as possible by the rejection of the densest images. Third, the intensity distribution error. This fortunately enters to a very small extent in this particular case, as the image of one component in single order condition lies very nearly between the two images of the other in double order condition, as mentioned on page 274.

The visual and microphotometer values are listed in Tables VI and VII respectively. No good tracings could be obtained for Hγ as the images were poor. The weighted means are calculated as in Table IV.

TABLE VI

Visual measurements of Δλ from echelon plates.

Line	Plate No.	Current ma/cm²	Character of image	Δλ* (Angstroms)	Means	Weighted means
H_α	E 8a	24	faint	0.1338		
	E 8b	24	faint	.1354	0.1367	
	E 6b	24	medium	.1386		
	E 7a	24	medium	.1388		0.136₃
	E35a	25	faint	.1305	0.1353	
			medium	.1400		
	E21a	23	faint	.1349	0.1365	
			medium	.1381		
$H\beta$	E22	23	medium	0.0771		
	E10b	24	medium	.0772	0.0774	
	E11b	24	medium	.0779		
	E 9b	24	dense	.0794	0.0794	0.079₄
	E38b	25	dense	.0818		
				.0826	0.0813	
				.0799		
$H\gamma$	E12b	25	faint	.0644	0.0637	
	E35b	25	faint	.0630		0.067₂
	E38b	25	medium	.0713	0.0707	
			medium	.0701		

* The agreement between different determinations of Δλ from the same plate is such that four decimals may be saved.

TABLE VII

Microphotometer measurements of Δλ from echelon plates.

Line	Tracing No.	Plate No.	Character of image	Δλ(A) (meas.)	Saddle height	Correction	True Δλ	Means	Weighted means
H_α	1(1)	E21a	faint	0.1332	57	1.45	0.1351		
	(2)		faint	.1310	51	.95	.1322	0.1338	
	(3)		faint	.1325	55	1.25	.1342		
	2(8)		medium	.1321	71	4.1	.1375	0.1371	
	(10)		medium	.1324	67	3.1	.1367		
	2(5)	E35a	medium	.1297	82.8	9.6	.1422		0.137₃
	(6)		medium	.1306	80.9	8.3	.1414	0.1413	
	(7)		medium	.1297	79.9	7.7	.1404		
	II*(a)	E 8a	faint	.1356	65.5	2.8	.1394		
	(b)		faint	.1330	63.3	2.3	.1361	0.1269	
	(c)		faint	.1310	66.8	3.1	.1351		
$H\beta$	IV†(d)	E38(b)	dense	0.0749	86.8	15	0.0799		
					81.2	8.5		0.0785	0.078₄
	(e)		dense	.0744	86.7	14.7	.0771		
					84.6	11.2			

* Mount Wilson microphotometer: very reliable tracings.

† As both saddle heights were high, but unequal, two corrections were made and their difference taken.

In calculating the final means from the values obtained by the Lummer plate system and the echelon we feel, first, that we are justified in rejecting entirely, for reasons previously stated, the microphotometer results of the crossed Lummer plate system; and, second, that the relative weights we

should assign are: 3 to the Lummer plate visual measurements, *although visual* (both because of the greater dispersion of the instrument and the greater number of determinations), 1 to the visual and 2 to the microphotometer values obtained with the echelon. These weighted means are given in Table VIII.

TABLE VIII

Final results for the doublet separations of H_α, $H\beta$, $H\gamma$. Weighted means of $\Delta\lambda$ and the corresponding values of $\Delta\nu$ obtained under the conditions of tube diameter, of pressure, and of temperature specified in the text.

Line	Mean values given in Table No.:	Lummer plate system visual	Echelon visual	Echelon microphotometer	Weighted means of $\Delta\lambda$(A)	$\Delta\nu$ (cm^{-1})
$H\alpha$	IV	0.1371				
	VI		0.1363		$0.137_0 \pm 0.001$	0.318 ± 0.002
	VII			0.1373		
$H\beta$	IV	0.0794				
	VI		0.0794		$0.079_1 \pm 0.001$	0.335 ± 0.002
	VII			0.0785		
$H\gamma$	(in text)	0.0664				
	VI		0.0672		$0.066_8 \pm 0.002$	0.353 ± 0.004

The theoretical values of $\Delta\nu$ on the old quantum theory are given in Table IX. With them are also tabulated the values predicted by the new quantum mechanics, with the spinning electron, based on the intensities given by Sommerfeld and Unsöld.[19] To these are added the experimental results obtained by Houston and the writers. The observations agree better with

TABLE IX

Doublet separations, $\Delta\nu$, theoretical and observed, of H_α, $H\beta$, and $H\gamma$.

		H_α	$H\beta$	$H\gamma$
Theoretical	Old quantum theory*	0.328	0.350	0.357
	New quantum mechanics, with spinning electron	.320	.345	.354
Observed	Houston	.315	.331	.353
	Kent, Pearson and Taylor	.318 (.323)†	.335	.354

* These values follow on the Bohr-Kramers' theory without an electric field and neglecting component c'' of Fig. 7. See Birge, Phys. Rev. **17**, 594 (1921).
† At low current density.

the new theory. Houston's results we regard as the most accurate hitherto obtained. Our values are somewhat larger. He, however, used a large current density. A change of $\Delta\lambda$ with current density would explain the result given by plate *L*30 (see Table IV) taken at but 13 ma./sq.cm. and giving, for $H\alpha$, $\Delta\lambda = 0.1391$A and $\Delta\nu = 0.323$ cm^{-1}.

It will be noted that the theoretical value for $H\beta$ on the new theory is greater than those observed by both Houston and us by an amount greater than the experimental error.

[19] A. Sommerfeld and A. Unsöld, Zeits. f. Physik. 237 (1926).

II. *Fine structure.* The new quantum mechanics with the spinning electron gives, at the hand of Sommerfeld and Unsöld, for Hα, Hβ and Hγ, structure and relative intensities as shown in Fig. 7.

The Lummer plate images of Hα, on the original negatives and under the proper photographic exposure conditions, show repeatedly a consider-

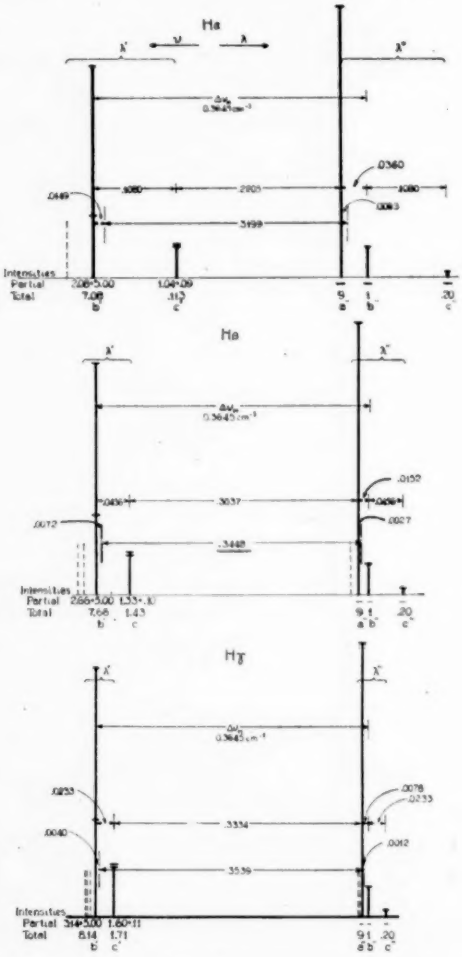


Fig. 7

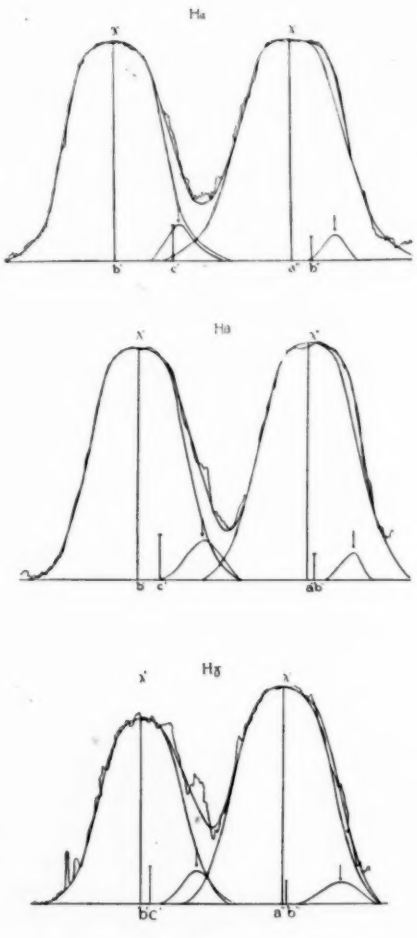


Fig. 8

Fig. 7. Theoretical structure according to the new quantum mechanics, with the spinning electron. The intensities given for Hγ are approximate.

Fig. 8. Microphotometer curves obtained from *enlargements* of the original negatives. For Hα, plate *L*7, order 12, E-W line 7*D*; for Hβ, plate *L*12, order 10, E-W line 7*D*; for Hγ, plate *L*21, order 3, E-W line 6*F* (a dense plate). Not much emphasis should be placed upon *b*″ in Hγ as constructed. λ″ is nearly symmetrical.

able extension of the long wave-length end of λ′. This is visible to the unaided eye in enlargements (see Plate II) and is undoubtedly due to the fine structure component, *c*′, of Fig. 7—clearly present although unresolved. An homologous extension exists in Hβ and Hγ.

On this theory we need not have recourse to the Stark effect to explain the presence of this component. λ′ has indeed been shown to be partially polarized, but the new theory has not yet advanced sufficiently to justify any definite statement as to the cause of this polarization.

In the microphotometer study of the structure, to obtain sufficient light, enlargements of the original, negatives were first used. The negative was run in the direction *mm′* of Fig. 6. The curves of Fig. 8 were obtained as follows: Graph paper was placed over the microphotometer negative and the original curve traced in, free hand. From the upper portion of λ′, the λ′ axis was determined and the longer wave-length slope of the curve constructed. With λ″ the top of the curve is unsymmetrical and the axis was here determined from a region about two-thirds the way down. The longer wave-length slope of λ″ was then drawn. By subtracting ordinates the curves for *c′* and *b″* were obtained.

It will be noticed, however, that the peaks of these three curves are all flattened at the top, that the weaker doublet component is stronger than theory demands (see Table X for theoretical ratio) and in all cases, except that of *c′* in Hα, the observed satellite lies much too far from the main line.

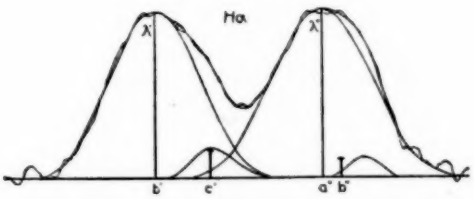


Fig. 9. Microphotometer curve from an original negative of Hα, plate *L*7, order 12, E-W line 1*D* (a rather dense image).

Over-exposure would produce just these three effects. The curves are, however, reproduced as an illustration of the different types of assymmetry in λ′ and λ″ and as an indication of the probable existence of fine structure. It may be shown that at liquid air temperature the theoretical half-widths of *b′* and *c′* in Hα are about equal to their separation. Therefore in even this most favorable case resolution would be impossible at that temperature.

As it was thought that the processes of enlargement produced the enhancement, tracings were made of adjacent images on the original negative. Fig. 9, however, shows that the photographic distortion enters somewhat even here. We were thus forced to use lower and fainter orders despite the effect of plate grain.

These final curves for Hα and Hβ are shown in Fig. 10. As less photographic distortion was here present, the following more accurate method of drawing the curves could be employed: By trial the height, half-width and position of the curve for *b′* was determined. Using the same half-width for *a″*, its height and position were obtained. The horizontal scale between *b′* and *a″* was thus found, Δν being, as in Fig. 7, 0.3285 and 0.3493 for Hα and Hβ respectively. The theoretical positions of *c′*, *b″* and *c″* were then

determined. The theoretical intensity ratios, $b':a''$ (see Table X), could not be used because of the intensity distortion produced by the Lummer plate, but *within* each component of the doublet the theoretical relative intensities *were* assigned.

From the equation $I = I_o e^{-z^2}$ experimental curves for the five components were then plotted and the sums of the ordinates taken. The resultant curve fits the irregular microphotometer trace fairly well for both Hα and Hβ.

The theoretical half-widths for Hα and Hβ, at liquid air temperature, are 0.051 and 0.038; those used by us are 0.079 and 0.058A respectively. This indicates 175° absolute, instead of 78°, as the effective temperature in the tube, which is probably not far from the truth, as the tube was run continuously and the capillary was of rather large (1 cm) diameter. Further-

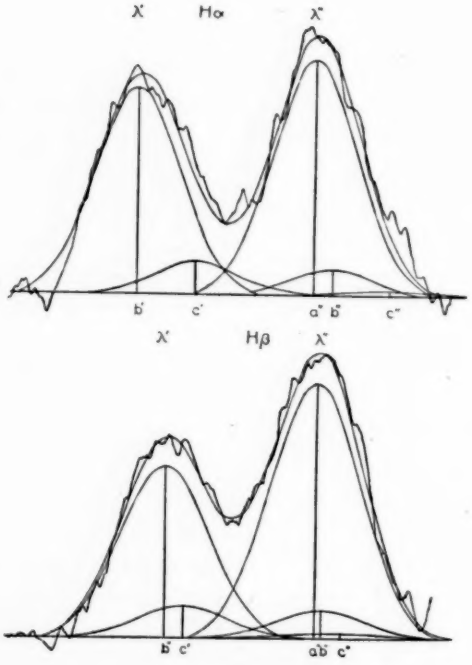


Fig. 10. Microphotometer curves from original negatives, faint images. For Hα, plate L 7 order 4, E-W line 6*D*; for Hβ, plate L 12, order 4, E-W line 13*D*.

more the scale of the negative is not strictly normal as assumed in our construction, and finally the microphotometer curves do not indicate true intensities. Despite these facts, we feel justified in stating that with Hα and Hβ the resultant curves are not inconsistent with the presence of the five components given by the new quantum mechanics with the spinning electron. Of the presence of c' we are certain; we are reasonably sure of b''; and, lastly, the resultant curves fit the case better *with* c'' than without it.

To Dr. Houston of the California Institute of Technology we are indebted for the facts concerning the interferometer presented in Table I, for valuable

suggestions in connection with corrections made in evaluating our plates, for the calculation of the intensity relations given in Fig. 7 and for his cordial and able assistance, generously given. We must record also our great indebtedness to our various assistants, especially Messrs. Handy, Hartwell and Ireland.

TABLE X

Intensity ratios, $I_{\lambda''}$, $I_{\lambda'}$, *of the components of the doublets*—illustrating the effects of not only the intensity distribution of the Lummer plate but also over-exposure.

Line	Theoretical ratio	Observed Ratio: Denser images or higher orders	From figure:—	Fainter images or lower Orders	From figure:—
H_α	1.24:1	1.01:1	9	1.07:1	10
		1.01:1	10		
$H\beta$	1.12:1	1.02:1	9	1.43:1	
$H\gamma$	1.03:1	—	—	1.02:1	8

This research was made possible by grants from the Rumford Committee of the American Academy of Arts and Sciences; this aid we most gratefully acknowledge. The work was begun at Boston University and completed at Mount Wilson Observatory and the California Institute of Technology in March 1927. To the last two institutions we are deeply indebted for the great facilities placed at our disposal.

BOSTON UNIVERSITY,
April. 1927.

THE INTENSITY RATIO OF THE BLUE CAESIUM DOUBLET

By C. F. Hagenow and A. Ll. Hughes

Abstract

The rule of Burger and Dorgelo leads one to expect a ratio of 2:1 for the intensities of the members of the blue doublet of caesium (4555, 4593A), a ratio which is in agreement with some experimental determinations and in disagreement with others. The new method of measuring intensities of spectral lines developed by Merton was employed in this investigation. The results gave ratios ranging from 2.3:1 to 3.8:1, the higher ratios being obtained with more attenuated sources where one would expect from Burger and Dorgelo's rule an asymptotic approach to the 2:1 ratio. As a check on the method the 2:1 ratio generally accepted for the potassium doublet (4044, 4047A) was verified.

THE intensity rule of Burger and Dorgelo[1] states that for the components of multiple spectral lines of the principal series the intensity ratio is equal to the ratio of the inner quantum numbers of the initial levels of the atoms. Thus this ratio should be 2:1 for the alkali metals.

This rule was verified by H. Jakob[2] in the case of doublets of higher members for potassium, rubidium and caesium. Dorgelo[3] found ratios ranging between 100:48 and 100:55 for the caesium doublet 4555, 4593A. However, a number of other observers find values quite at variance with this rule. Filippov[4] has an average intensity ratio of 3.81:1 for the blue caesium doublet when the weakest possible concentration of the salt was used. He states that this is in good agreement with the ratio of 4:1 found by Roschdestwensky.[5] When an arc formed by salt impregnated carbons was employed, Filippov obtained intensity ratios varying from 1.81:1 to 3.2:1, the higher ratios corresponding to smaller concentrations. For large concentrations his results agree with those of Dorgelo and Oudt,[6] but not for small concentrations. Thus he finds that, in general, the intensity ratio diminishes with increasing concentration, whereas Dorgelo,[7] after remarking that these measurements are rendered difficult on account of self-reversal, states that "the less the density of the emitting gases, the more does the intensity ratio of the components of the doublets of the principal series approach the value of 2:1."

For the same caesium doublet Kohn and Jakob[8] obtain values of the intensity ratio ranging from 3.43:1 to 4.25:1. Füchtbauer[9] concludes that

[1] H. C. Burger and H. B. Dorgelo, Zeits. f. Physik. **23**, 258 (1924).
[2] H. Jakob, Naturwissenschaften **13**, 906 (1925).
[3] H. B. Dorgelo, Dissertation, Utrecht (1924).
[4] A. Filippov, Zeits. f. Physik. **36**, 477 (1926).
[5] D. S. Roschdestwensky, Trans. Opt. Inst. Petrograd; **2**, No. 13, Berlin (1921).
[6] F. W. Oudt, Zeits. f. Physik. **33**, 656 (1925).
[7] H. B. Dorgelo, Phys. Zeits. **26**, 783 (1925).
[8] H. Kohn and H. Jakob, Phys. Zeits. **27**, 819 (1926).
[9] Chr. Füchtbauer, Phys. Zeits. **27**, 853 (1926).

a constant intensity ratio of 2:1 is irreconcilable with the experimental evidence, and that the intensity ratio of this caesium doublet increases markedly with increasing quantum number. Roschdestwensky found values equal to 2:1, 7:1, and 9:1 for caesium doublets $1s$–$2p$, $1s$–$4p$ and $1s$–$5p$, respectively.

The following is an account of a number of intensity measurements on the blue doublet of caesium, as well as some on the potassium doublet 4044, 4047A, the results of which are in close agreement with those of Filippov and of Kohn and Jakob.

The intensity ratios were measured by means of a recent method devised by Merton.[10] This method requires, in addition to a neutral optical wedge, a special screen consisting of a series of parallel, alternately transparent and opaque strips (ruled on glass or other transparent material by a method presently to be described) which is placed directly before the slit of the spectrograph with the strips at right angles to the slit. Next to this comes the optical wedge, so that the slit, screen and wedge are practically in contact each with the next.

This screen was constructed as follows: An engraver's screen was photographed on glass, suitably reduced. In this case the clear strips were 0.04 mm wide, which is also exactly the width of the slit, and they were spaced about five to the millimeter. The sensitive film was then peeled from the glass and mounted on thin celluloid, a small piece of which was placed before the slit of the spectrograph as described above.

A photograph of a continuous spectrum taken through the wedge and screen will show the spectrum crossed by a series of horizontal rulings diminishing in density toward the thick end of the wedge. If now a photograph of the spectral lines under investigation, taken through the *unobstructed* slit, be superposed on the continuous spectrum, it is evident that among the horizontal rulings one will be found to match the given spectral line in density. Or, for greater accuracy, an interpolation method, using a microphotometer, may be applied in the neighborhood of a match, as was done in a number of cases in these experiments. The density gradient of the wedge as a function of the wave-length was also found very conveniently by means of the rulings.[10]

The ratio of the intensities of two lines, λ_1 and λ_2, is then given by the expression, deduced by Merton,

$$\frac{I_1}{I_2}=\frac{c_1(\lambda_1-\lambda_0)}{\log_{10} n_1 d_1}\div\frac{c_2(\lambda_2-\lambda_0)}{\log_{10} n_2 d_2},$$

where λ_0 is the constant of Hartman's formula, c the intensity of the continuous spectrum, d the density gradient of the wedge per line of the rulings, and n the number of the rulings from some fiducial line to the match. It is evident from the above expression that the ratio of two intensities depends merely on the difference between n_1 and n_2. The crater of a carbon arc

[10] T. R. Merton, Proc. Roy. Soc. **113**, 697 (1927).

furnished the continuous spectrum and c was calculated from Planck's formula, using 3750°, absolute, as the temperature of the crater.

Care was taken to see that the slit was uniformly illuminated by whatever source used, which is essential in this method. In the region of the plate actually used in matching the spectral lines with the rulings, the discrepancy found by examination with a microphotometer amounted to never more than about 4 percent. This is probably within the accuracy of the plate itself.

Three methods of exciting the luminosity of caesium were used: caesium chloride in a bunsen flame either on a piece of platinum foil or as a sprayed solution, and in a carbon arc. The present method was not adapted to an exact measurement of the concentration of the salt solution employed, but the concentration varied from normal to twice that amount. Low concentrations were not used on account of the lack of luminosity. It was noticed that changes of concentration of the spray in the flame did not seem to affect the results. Table I is a survey of the results for the blue doublet of caesium.

TABLE I

Intensity ratio in the blue doublet of caesium.

No. of plate	Source	Intensity ratio	
		Matching by inspection	Matching by microphotometer
1	Spray in flame	3.87	
2	" " "	3.74	
3	" " "	3.31	3.58
4	Salt on Pt. foil	3.06	
5	" " " "	2.72	2.77
6	Salt in arc	2.41	2.75
7	" " "	2.41	2.53
8	" " "	2.24	2.40
9	" " "	2.24	2.55

The third column contains the values of the intensity ratios of the components of the blue caesium doublet as found by visual matching. These values are, generally, the averages of the readings of two spectra on the same plate. The individual differences were as large in a few cases as those between the numbers in the third and fourth columns. The values in the fourth column were obtained by an interpolation method, using the microphotometer. In this way, instead of having to decide on some one ruling as an exact match to the given spectral line, it was possible to interpolate between two rulings by taking density readings on the rulings in the neighborhood of a match.

It is seen that the intensity ratios are much less in the arc, and slightly less in the flame when the salt is introduced directly, than when the salt is sprayed in, which is in accordance with the findings of Filippov. An estimate of the relative intensity of the sources shows that, taking them in the order shown in Table I, they are roughly in the ratio of 1:20:400. Filippov's average value, over all concentrations, is 3.54:1, which may be compared with the valued 3.58 in the table above, probably the most reliable, all

things considered. However, this very close agreement must be considered largely accidental.

As the intensity ratios of sodium and potassium are much better established, some measurements were made on the potassium doublet 4044, 4047A as a check on the accuracy of the method. The matching of the lines was done visually only, with the results as shown in Table II. The concentrations of the sprayed solutions varied from twice to eight times normal, with no apparent correlation with the intensity ratios observed. These values agree well with those of many earlier investigators.

TABLE II

Intensity ratios in the potassium doublet.

No. of plate	Source	Intensity ratio
1	Spray in flame	2.10
2	" " "	1.92
3	" " "	2.00
4	" " "	1.92

Our results for the blue doublet of caesium furnish additional evidence in favor of an intensity ratio decidedly larger than 2:1 for this doublet.

WASHINGTON UNIVERSITY,
ST. LOUIS, MISSOURI.
June 25, 1927.

THE QUENCHING OF MERCURY RESONANCE RADIATION BY FOREIGN GASES*

By Paul D. Foote

Abstract

The intensity of emitted resonance radiation from Hg vapor is decreased as the pressure of an admixed gas increases. The following cycle of transitions occurs for the rare gases or nitrogen. Absorption of λ2537 produces $^3P_1$ Hg′ atoms. Some of these return to the $1S_0$ state by radiating and a portion of this radiation escapes to be observed as resonance. The rest is reabsorbed in the vapor producing more $^3P_1$ atoms. Some of the $^3P_1$ atoms undergo collision of the second type with foreign gas molecules resulting in $^3P_0$ atoms. A large fraction of these atoms return to the $^3P_1$ state by collision of the first type with high speed gas molecules. At 18°C one collision in 6000 satisfies the condition of conservation of energy and momentum requisite to such an energy transfer. Other $^3P_0$ atoms return to the normal state through collision with traces of hydrogen impurities in which the energy of the mercury atom is utilized in the dissociation of H_2. Still other $^3P_0$ atoms collide with normal Hg atoms producing Hg_2′ excited molecules. This cycle of transitions is completely developed from kinetic theory considerations in which every collision, except in the molecular formation, is considered as effective. All the constants may be computed directly. Concentrations of the $^3P_0$ state as high as one part in a few hundred may be readily obtained under moderately intense illumination.

THE intensity of the resonance radiation from mercury vapor at room temperature, excited by a resonance lamp, rapidly diminishes as the pressure of an admixed gas is increased.[1] A quantitative interpretation of the processes occurring, however, has heretofore not been very satisfactory. In connection with some work on fluorescence and photo-ionization of mercury vapor which the writer has in progress, it was necessary to consider more carefully the mechanism of the resonance quenching.

Hydrogen is especially effective for quenching mercury resonance, a pressure of about 0.2 mm being sufficient to reduce the intensity of the λ2537 emission to one-half its value without the foreign gas. A normal mercury atom absorbs a quantum of the incident λ2537 radiation and if, during its life in the 2^3P_1 state it collides with a hydrogen molecule, the latter is dissociated. The energy otherwise available for radiation is used mainly in the work of dissociation, the small amount of energy remaining over going into kinetic energy, for the most part, of the hydrogen atoms. From simple kinetic theory, one may compute the pressure p of the admixed gas which is necessary in order that the probability of a collision between a 2^3P_1 atom and a gas molecule be equal to the probability that the excited

* Published with the approval of the Director of the Bureau of Standards of the U. S. Department of Commerce.

[1] Stuart, Zeits. f. Physik. **32**, p. 262 (1925).
Cario and Franck, *idem* **37**, p. 619 (1926).

Hg atom radiates during the mean life $\tau = 1.1 \cdot 10^{-7}$ sec. in the undisturbed state, as follows:

$$p = \frac{3.84 \cdot 10^{-23}}{\sigma^2 \tau} \left(\frac{M_1 M_2}{M_1 + M_2} \right)^{1/2}. \qquad (1)$$

In this equation p is the pressure in mm Hg, M_1, the molecular weight of Hg, M_2 that of the foreign gas, and σ the sum of the radii of the two colliding molecules, the temperature being 18°C. Assuming every collision effective in quenching, and that this is the only effect of the foreign gas, and neglecting the absorption, within the resonance bulb, of the emitted resonance radiation, Eq. (1) should give the pressure at which the intensity of the resonance radiation is reduced to half its value without the admixed gas. Actually, these assumptions require considerable modification.

The statistical processes occurring in the quenching by H_2 may be illustrated by Fig. 1*a*. The number of transitions per sec. from 1^1S_0 to 2^3P_1

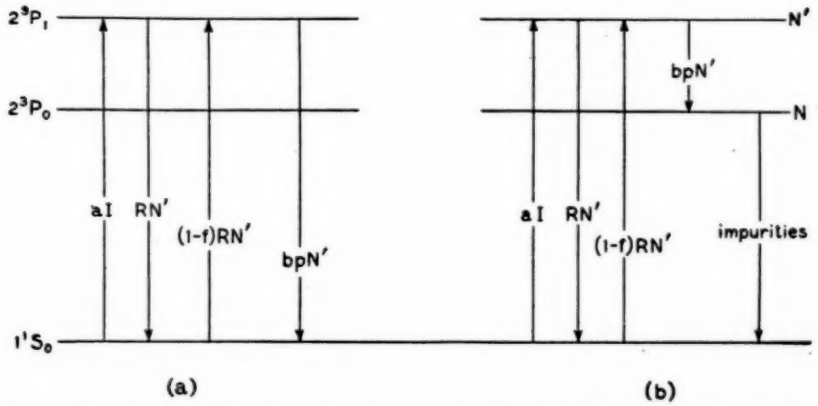


Fig. 1. (*a*) Quenching by H_2. (*b*) Analogous diagram for quenching by rare gases.

is equal to a constant a times the intensity I of the incident monochromatic illumination. This assumes that the added gas does not seriously change the amount of energy absorbed by the resonance cell. In the first place, the Lorentz broadening of the absorption line at gas pressures ranging from zero to one or two hundred mm Hg, is certainly small compared with the Doppler broadening and especially to the coupled damping influence[2] of the other Hg atoms to which the vapor is astonishingly sensitive. Direct experiments on the Lorentz broadening are performed at pressures of many atmospheres where the effect becomes measurable. Secondly as the absorption line is broadened, the absorption coefficient at the maximum decreases so that with a source representing a constant spectral distribution, the relative increase in total absorbed energy is less than the relative increase in Lorentz broadening. Finally in Stuart's experiments, the source was itself a resonance lamp and the resonance cell was deep enough to absorb all the energy incident

[2] Holtsmark, Zeits. f. Physik. **34**, p. 722 (1925). Trumpy *idem.* **34**, p. 715 (1925); **40**, p. 594 (1926).

upon it. Merely the depth of penetration should be therefore increased slightly by the foreign gas while the total number of quanta absorbed remains unchanged. Accordingly, in any of the ordinary resonance experiments, it does not appear necessary to consider a as a function of the pressure although this could be readily done if desired.

Some of the atoms in the 2^3P_1 state radiate, and the number of radiating transitions is equal to a constant R times the population N' of the 2^3P_1 level. Other Hg′ atoms collide with H_2 molecules, the number of such transitions being the product of a constant b, the pressure p of the added gas, and the population N'. Of the total RN' quanta emitted by the vapor per sec., let the fraction f escape from the bulb as resonance radiation while the amount $(1-f)RN'$ is reabsorbed. Then for equilibrium we have

$$aI+(1-f)RN'=RN'+bpN'. \tag{2}$$

The intensity J of the resonance radiation is proportional to fRN': let $fRN'=gJ$ where g is a constant. On choosing the scale for intensity of resonance such that $J=100$ when $p=0$, we obtain from Eq. (2)

$$J=100/(1+bp/fR) \tag{3}$$

for the relation between the intensity of the resonance radiation and the pressure of the admixed H_2. Stuart's data at 18°C furnish an empirical evaluation of $b/fR=4.6$. Using this constant, the J *vs.* p relation is plotted in Fig. 4, according to Eq. (3) while the dots represent the observations.

At a pressure such that $bp/fR=1$ (i.e., $p=0.217$ mm) the resonance radiation is reduced to half its initial value while at a somewhat greater pressure $p=0.217/f$, where $bp/R=1$, there is equal probability that a Hg′ atom radiates or collides with a H_2 molecule. This latter pressure, and hence f, could be computed directly from Eq. (1) if the effective radius of the Hg′ atom were known. However, the quantity f may be estimated in another manner. In Stuart's experiments the radiation was directed on one face of the resonance cell and the intensity of radiation emitted back through the same face in a direction nearly symmetrical to the incident beam was measured photographically. Let $E=E_0e^{-\mu x}$ be the energy flux at any depth x along the beam within the resonance cell. The rate of absorption of energy at the point x is accordingly $dE=\mu E_0e^{-\mu x}dx$. The rate at which the absorbed energy returns from this point to the front of the cell is $KdEe^{-\mu x}$ where K is a constant depending on the geometry of the apparatus. Integrating this from $x=0$ to ∞ one obtains $0.5KE_0$. If there had been no absorption on the way out, the escaping energy rate would have been KE_0. A second approximation for f involves consideration of the secondary resonance excited by the primary emission, but this first approximation appears sufficiently accurate for the present. As will be evident later, the only error introduced in the following discussion by an incomplete evaluation of f is of a differential nature arising in the fact that the kinetic theory radii of various gases differ slightly.

Using $f=0.5$, the hydrogen pressure for equal probability of radiation or impact is 0.434 mm. Substituting this in Eq. (1) and assuming the kinetic theory radius for H_2 ($\sigma_1=1.34\cdot10^{-8}$) we obtain $\sigma_2=2.03\cdot10^{-8}$ cm for the radius of the Hg′ atom. The kinetic theory value for the unexcited atom Hg is $1.75\cdot10^{-8}$ which is somewhat smaller than the above computed radius, as should be expected. With $\sigma_2=2.03\cdot10^{-8}$ and the accepted kinetic theory radii for the foreign gases one may compute by Eq. (1) the value of the constant b/R, the reciprocal of which is numerically equal to the pressure in mm at which there is equal probability for the Hg′ atom to radiate or to collide. These data are summarized in Table I.

TABLE I

Kinetic theory data.

Gas	Radius	Type of collision	b/R	b/fR
Hg	$1.75\cdot10^{-8}$	Hg′−Hg	0.41	0.82
H_2	1.34	Hg′−H_2	2.3	4.6
N_2	1.90	Hg′−N_2	0.89	1.78
He	1.11	Hg′−He	1.42	2.84
A	1.81	Hg′−A	0.74	1.48
Hg′	2.03			

Quenching by gases which have no critical potential below the 4.9 volt point of mercury takes place in a manner different from that described for H_2. At collision the 2^3P_1 atom drops to the 2^3P_0 metastable state giving up an energy equivalent to 0.218 volts which is dissipated mainly as kinetic energy of the lighter foreign gas molecule. The number of such transitions occurring per sec. is bpN' as shown in Fig. 1*b*. It has always been assumed that at room temperature no appreciable number of reverse transitions from $^3P_0$ to $^3P_1$ occurs; hence the quenching should not be concerned with the population N of the former state. It is sufficient that the slightest trace of impurity such as H_2 will prevent an extremely high concentration of this long-lived metastable state through collisions leading to dissociation. The relation between J and p therefore should be of the form given by Eq. (3).

If this relation is applied to Stuart's data, the values of fR/b increase very rapidly with the pressure as shown in Fig. 2. It seems quite reasonable that the small values of fR/b, which the curves tend to approach at low pressure (not distinguishable from zero on the large scale of this figure), are the kinetic theory constants as given in Table I. Stuart considered only the constant at the pressure corresponding to 50 percent quenching and finding that the experimentally observed pressures were up to 300 times those computed by Eq. (1), concluded that each gas possessed an efficiency coefficient for an effective quenching collision. The variation of these coefficients, however, is much more marked for the same gas at different pressures. Thus, if we adopt this interpretation, the coefficient for helium varies from 0.00054 at 230 mm to values approaching unity near zero pressure. The form of the curves of Fig. 2 suggests that the collisions are

always effective but that another process is occurring which partially offsets the rapid quenching on the basis of 100 percent efficiency. This process consists in the upward transitions $^3P_0 \rightarrow {}^3P_1$ produced by collisions between the metastable Hg′ atoms and fast gas molecules.

In a mixture, therefore, of two gases, Hg′ and the foreign gas, it is necessary to know the fractional number of collisions between the two different types of molecule for which the available kinetic energy is sufficient to effect the transition $^3P_0 \rightarrow {}^3P_1$. We shall omit consideration of the change in angular

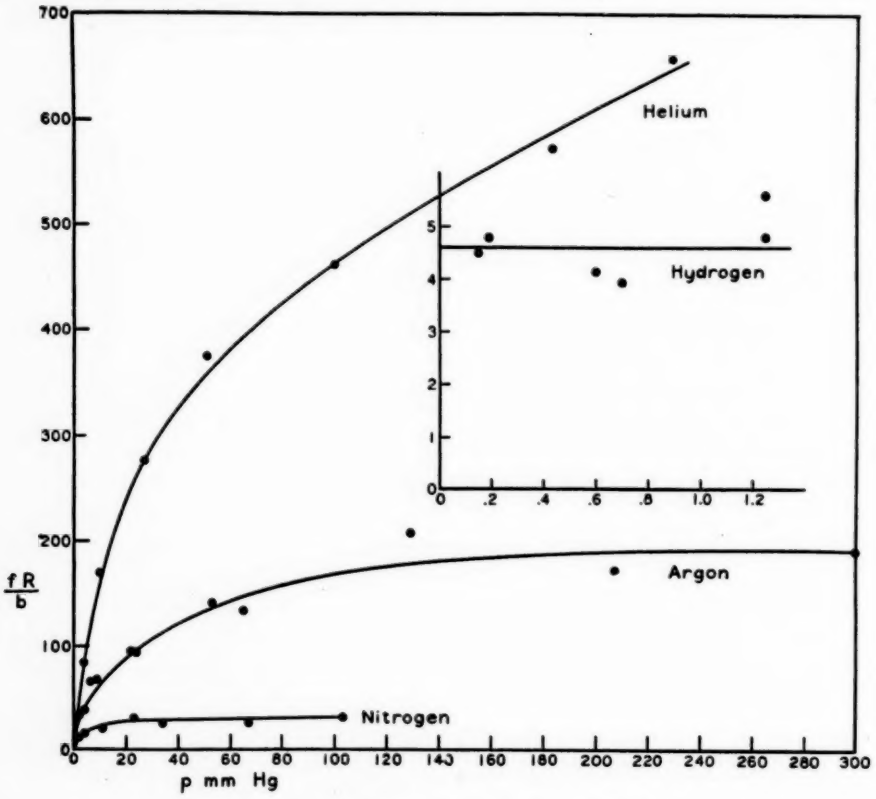


Fig. 2. Values of fR/b on scheme shown by Fig. 2*b*.

momentum of the Hg′ atom and, as is customary in problems connected with the kinetic theory of chemical reactions, shall assume that only the component of the relative velocity of the two impacting atoms, resolved along the line of centers, is effective. The total number of all collisions per sec. between the two different kinds of molecule, n_1 of absolute mass m_1 and n_2 of mass m_2 is given[3] by Eq. (4)

$$\text{Total number of collisions per sec} = 2\sigma^2 n_1 n_2 \left[\frac{2\pi kT(m_1+m_2)}{m_1 m_2}\right]^{1/2} \qquad (4)$$

[3] This equation and Eq. (5) are derived in detail by Tolman, Statistical Mechanics, p. 69, Chemical Catalog Co.

where $k=1.372\cdot10^{-16}$ erg deg^{-1}. The fractional part F of these in which the component of relative velocity parallel to the line of centers is greater than R_0 is

$$F=e^{-\frac{m_1m_2}{m_1+m_2}\frac{R_0}{2kT}}. \tag{5}$$

Let ϵ_0 = the energy difference between the $^3P_0$ and $^3P_1$ energy levels, i.e., $3.47\cdot10^{-13}$ ergs corresponding to 0.218 volts. In order that conservation of energy and linear momentum obtain, the collision must be subject to the condition

$$R_0^2=2\epsilon_0(m_1+m_2)/m_1m_2. \tag{6}$$

Substituting this in Eq. (5) we find

$$F=e^{-x} \text{ where } x=\epsilon_0/kT. \tag{7}$$

The fractional number of collisions capable of effecting the upward transition $^3P_0\rightarrow{}^3P_1$ is therefore independent of the nature of the added gas.

The application of Eq. (7) furnishes an interesting picture for the quantum theory distribution of excited states. For example, consider the atoms belonging to Group III of the periodic table where we have two low-lying metastable ^2P terms. Assume n atoms in the normal state and m in the higher level. The number of transitions per sec. from n to m is $Fbpn$, where Fbp represents the collision rate with fast atoms, while the number of transitions from m to n equals bpm. Equating for equilibrium, we find $m/n=F=e^{-x}$ where $x=\epsilon_0/kT$ in agreement with the ordinary quantum theory derivation. Indeed, it might have been more logical to have approached the problem solely from this standpoint thus avoiding the question of what constitutes an effective collision.

Values of F for several temperatures are as follows:

t°C:	18	20	25	750
F:	0.000168	0.000177	0.000206	0.0846

Thus at 18°C, out of every 6000 collisions there is one in which the transfer of kinetic energy is sufficient to produce the transition from $^3P_0$ to $^3P_1$. Hence, if the life of the metastable state, which is terminated by collision with impurities, etc., were 6000 times that of the $^3P_1$ state[4] the probability that a $^3P_0$ atom collides with a high speed gas molecule should be the same as the probability that a $^3P_1$ atom makes any collision at all. It is therefore surprising that the importance of such upward transitions at room temperature has not been realized, especially in view of the work by Cario and Franck who found no quenching at 750°C where about one collision in twelve involves the requisite energy.

Every time a $^3P_0$ atom is lost by collision with an impurity a small amount of kinetic energy is communicated to the body of the gas, 0.218 volts in the transitions $^3P_1\rightarrow{}^3P_0$ and whatever energy remains after the dissociation process. The high speed molecules so produced, however, are directly ineffective. For example, at 10 mm gas pressure, a mercury pressure

[4] Experimental determinations frequently indicate a much longer life. Cf. Dorgelo, Physica **5**, p. 492 (1925).

of 0.0015 corresponding to 18°C, and an assumed concentration of $^3P_0$ atoms of 0.1 percent, any individual high speed gas atom on the average would make roughly twenty million collisions with other gas atoms before encountering a $^3P_0$ atom. During this time the Maxwellian distribution of velocities should be accurately established. Hence, such transitions result only in increasing the temperature of the gas by an amount which the writer found too small to be easily detected; certainly not enough to alter appreciably the value of F in the usual resonance radiation experiments.

If N be the population of the $^3P_0$ state, the product of a constant d, the pressure p, and N, represents the number of upward transitions occurring per sec. at a given temperature. In order to eliminate N from the relations it is necessary to know by what other processes the supply of $^3P_0$ atoms is exhausted. It has been generally assumed by Franck and his colleagues that collision between an excited and normal Hg atom results in a Hg_2' excited molecule. The number of such transitions may be represented by cN where c is a constant proportional to the pressure of Hg vapor. That such a process actually occurs is not definitely established. Probably there is no better evidence for its existence than the fact that it yields consistent results in the following derivation. The writer has some indirect evidence from work on fluorescence, with very intense illumination, that molecules consisting of two excited atoms may play a rôle in these quenching processes but for the present we shall assume that the probability of the collision of two excited atoms is small compared with that of an excited and normal atom, *a priori* an almost obvious conclusion since the concentration of excited atoms is small. A further important loss from the $^3P_0$ state is produced by a trace of impurity such as hydrogen. Thus at 10 mm gas pressure an impurity of a few parts in 10^5 should be as effectual in quenching by dissociation as

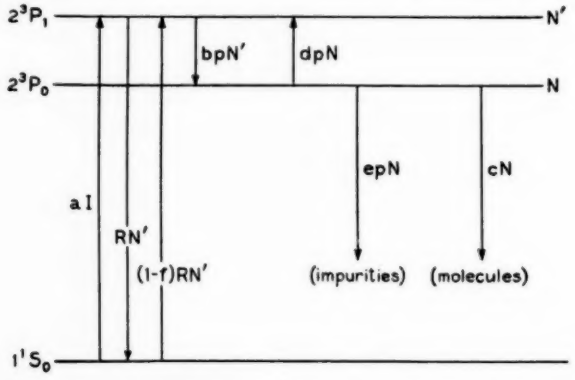


Fig. 3. Complete scheme for quenching by rare gases.

is the mercury vapor in quenching by molecular formation, assuming as usual 100 percent efficiency in all processes. The impurity loss may be represented by epN where e involves the ratio of the pressures of the impurity and of the gas as well as the collision rate. Small impurities have no effect on the $^3P_1$ state because of its short life.

The transition diagram for quenching by the rare gases, as discussed above, is shown in Fig. 3. Equating the number of transitions to and from each level, we obtain

$$aI+(1-f)RN'+dpN=bpN'+RN' \tag{8}$$

$$bpN'=dpN+cN+epN. \tag{9}$$

On eliminating N from these equations, putting $fRN'=gJ$, and letting $J=100$ when $p=0$ one finds

$$J=\frac{100}{\left[1+\dfrac{\left(\dfrac{c}{dp}+\dfrac{e}{d}\right)\dfrac{bp}{fR}}{1+\dfrac{c}{dp}+\dfrac{e}{d}}\right]} \tag{10}$$

This relation may be rectified by plotting the reciprocal of

$$\frac{b/fR}{(100/J)-1}-\frac{1}{p}$$

versus the pressure p. The slope of the straight line so obtained gives the value of e/d, and the intercept when $p=0$, the value of c/d. The first four columns of Table II summarize the constants for three gases based on

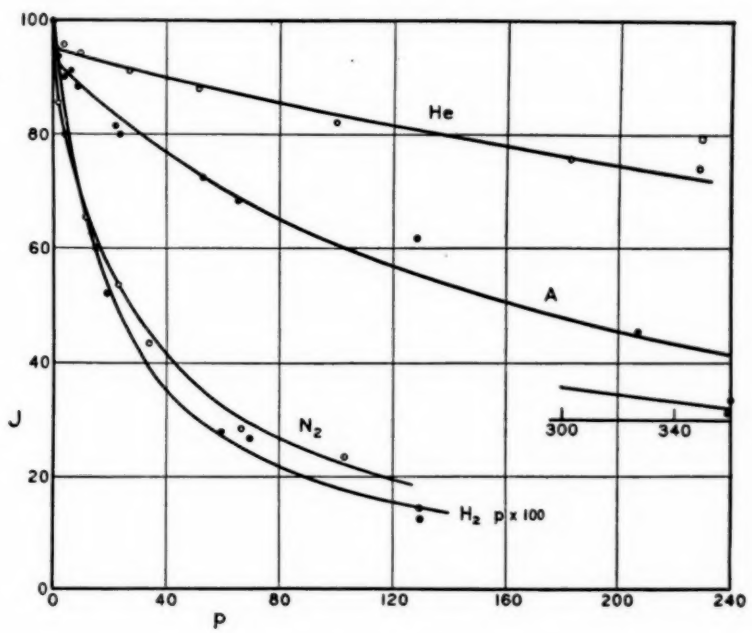


Fig. 4. Quenching by several gases. The full lines are drawn according to the theory and the plotted points represent Stuart's observations.

Stuart's data. In Fig. 4 the full lines are drawn in accordance with Eq. (10) while the plotted points represent the observations. No point deviates from the curves by more than the experimental error.

TABLE II

Quenching data.

Gas	c/d	e/d	b/fR	Impurity (H_2) 1 part in	c/d computed
He	.0180	.00051	2.84	18,000,000	2.6
N_2	.060	.0193	1.78	800,000	4.1
A	.050	.0039	1.48	4,900,000	5.1

It is possible to estimate the amount of impurity, considered as H_2, which was present in Stuart's experiments. The quantity epN represents the collision rate with the impurity at the pressure p' while dpN is the collision rate with fast gas atoms at the pressure p. Eq. (4) may be rewritten as follows:

$$\text{collision rate} = A p \sigma^2 [(M_1+M_2)/M_1M_2]^{1/2}$$

where A is a constant for a given temperature. Hence

$$Hg'-gas \quad dpN = AF_{18} p\sigma^2 [(M_1+M_2)/M_1M_2]^{1/2}$$
$$Hg'-H_2 \quad epN = Ap'(8.0)10^{-16}$$

$$\frac{p'}{p} = \frac{e}{d} \frac{F_{18}\sigma^2[(M_1+M_2)/M_1M_2]^{1/2}}{8.0 \cdot 10^{-16}}. \tag{11}$$

On substituting the values for the constants and determining σ from the data in Table I, the relative H_2 contents shown in column 5 of Table II are obtained. These values may not be unreasonable. One should expect high purity as indicated since special precautions were observed in handling the gas and especially since the radiation should exert a clean-up action.

It is especially interesting that the computed impurity in N_2 is at least as small as that likely to have been present. According to spectroscopic data the N_2 molecule is capable of absorbing vibrational energy in almost any amount up to several volts. Quenching of the $^3P_0$ state by such a process and the ultimate distribution of this energy as kinetic energy, since the vibrational states are radiationless, would be interpreted, in accordance with Fig. 3, simply as the effect of an impurity. We may therefore conclude that collisions in which the $^3P_0$ (or $^3P_1$) atom transfers energy to a vibrational state of the N_2 molecule are improbable. This may be also inferred from the fact that, according to Cario and Franck, there is no quenching of the $^3P_1$ state at 750°C.

The constant c/d possesses significance from the kinetic theory standpoint. We have: cN = rate of collision between Hg′ and Hg normal atoms at pressure 0.0015 mm while dpN = rate of collision between Hg′ and fast

gas molecules at pressure p. Whence by the same procedure as that used in deriving Eq. (11) one obtains

$$\frac{c}{d}=\frac{0.00215\cdot 10^{-16}}{F_{18}\sigma^2[(M_1+M_2)/M_1M_2]^{1/2}}. \tag{12}$$

Values of c/d so computed are given in column 6 of Table II. These are roughly 100 times the empirically determined constants. That the computed collision rate c should exceed the experimental data for molecular formation is precisely what may be expected from our knowledge of chemical reactions. As discussed by Tolman[5] no bimolecular reaction rate is known which even approaches the kinetic theory value. In the recombination of monatomic bromine one collision in about 1250 is effective, an efficiency of 0.1 percent. The reaction efficiency for the Hg_2' molecular formation of about 1 percent is therefore perhaps the highest efficiency yet observed for a bimolecular reaction. Such efficiencies may be interpreted as the result of an essential orientation of the colliding atoms but since nothing regarding the process is understood, we shall in the following discussion employ the empirical values of c/d as experimental facts.

The relative populations of the $^3P_0$ and $^3P_1$ levels may be determined by use of Eq. (9).

$$\frac{N}{N'}=\frac{b}{d}\,\frac{p}{p+\frac{c}{d}+\frac{e}{d}p}. \tag{13}$$

The quantity d/b is simply the fractional number of collisions between $^3P_0$ atoms and gas molecules in which the available kinetic energy is sufficient to effect the transition $^3P_0\rightarrow{}^3P_1$; that is $b/d=1/F=5950$ at 18°C. Thus for N_2 at the pressure p we find

$$N/N'=5950p/(1.02p+0.06)\cdot \tag{14}$$

The population ratio at 18°C is accordingly zero at zero pressure, rising rapidly within 1 or 2 mm gas pressure where it practically reaches the asymptotic value 5800. The intensity of the resonance radiation is proportional to the population N' and decreases with increasing pressure as shown by Fig. 4. Hence the population N of the metastable level rapidly increases from zero to a maximum at 1 or 2 mm (depending of course upon the impurity content) and then falls at approximately the same rate as the resonance radiation.

The data permit the evaluation of the mean life of the Hg' atom. Let t' be the mean life of the $^3P_1$ state. The population N' is equal to t' times the rate at which transitions occur to or from this state, or from Fig. 3:

$$N'=t'(RN'+bpN') \tag{15}$$

[5] Loc. cit., p. 242.

and

$$t'=\frac{1/R}{1+bp/R}. \tag{16}$$

But when $p=0$, $t'=\tau=1.1\cdot10^{-7}$ sec. so that $1/R=1.1\cdot10^{-7}$ and fR, to be used later, is equal to $4.54\cdot10^{6}$. Hence with N_2 gas present $t'=1.1\cdot10^{-7}/(1+0.89p)$. Thus the mean life t' with a moderate gas pressure may differ from τ by several orders of magnitude, a fact not always recognized. At 2 mm N_2 the life is $4\cdot10^{-8}$ sec.

Let t be the mean life of the $^3P_0$ state. The rate of supply for this state is bpN'. Accordingly $bpN't=N$ and

$$t=\frac{N}{N'}\cdot\frac{R}{b}\cdot\frac{1}{R}\cdot\frac{1}{p} \tag{17}$$

Thus for 2 mm N_2 the life of the metastable state is $t=3.5\cdot10^{-4}$ sec at 18°C, and for higher pressure the life is approximately inversely proportional to p.

If we knew the rate at which the Hg vapor absorbed quanta under a given stimulation it should be possible to estimate the actual concentrations of the $^3P_0$ and $^3P_1$ atoms. Precise measurements of this type are greatly needed. Qualitative observations made by the writer with the direct illumination from a water-cooled arc indicated that about 0.01 watt of λ2537 was absorbed by 10 cm³ of Hg vapor at 18°C, corresponding to $1.3\cdot10^{16}$ quanta/sec. In this amount of vapor there are $5\cdot10^{14}$ Hg atoms. Such illumination may be several hundred times that employed by Stuart but is probably of much less intensity than that used by Wood[5] in his experiments on "controlled orbital transitions." We shall see that the simple theory so far developed is not precisely applicable for such intense illumination but qualitatively it shows that very high concentrations of the metastable state are possible. It readily follows from Eqs. (8) and (9) that

$$N'=\frac{aI}{fR\left[1+\dfrac{bp}{fR}\dfrac{\dfrac{c}{d}+\dfrac{e}{d}p}{p+\dfrac{e}{d}p+\dfrac{c}{d}}\right]} \tag{18}$$

where $aI=1.3\cdot10^{16}$ quanta/sec. and all the constants are known. At 2mm N_2 we find $N'=2.45\cdot10^{9}$ and by Eq. (14) $N=1.39\cdot10^{13}$. Since there are 5.10^{14} Hg atoms, 1 atom in 204,000 is in the $^3P_1$ state and 1 atom in 36 is in the $^3P_0$ state. With so high a concentration of the $^3P_0$ state, collisions between metastable atoms become of importance and an additional loss hN^2 must be considered in the cycle of Fig. 3. The relations existing under high illumination will be discussed in a later paper in connection with fluorescence phenomena.

[5] Wood, Phil. Mag. **50**, p. 774 (1925).

Confining our attention to moderate illumination, the ratio of the number of downward to upward transitions bpN'/dpN produced by collision is of interest. From Eq. (13) it follows that

$$\frac{bpN'}{dpN}=1+\frac{e}{d}+\frac{c}{dp} \tag{19}$$

On substituting the values for the constants, one finds that, with N_2 at 2 mm, out of every 100 downward transitions 95 go back by collision with high speed molecules and 98 go back at a pressure of 100 mm. From Eqs. (8) and (13)

$$\frac{aI}{dpN}=\left(1+\frac{e}{d}+\frac{c}{dp}\right)\left(1+\frac{fR}{bp}\right)-1=0.343 \text{ for } p=2\text{mm}N_2 \tag{20}$$

Hence the number of transitions upward may exceed by far the total number of incident quanta because of the many transitions occurring back and forth between the $^3P_1$ and $^3P_0$ levels. As a specific example, we may consider 1000 incident quanta absorbed by the bulb of Hg vapor per sec. and a N_2 pressure of 2 mm. The following numerical values, corresponding to Fig. 3, are then obtained by the use of the formulas already given.

N_2 $p=2$ mm	bpN'	$=3060$	$epN=57$
Hg $p=0.0015$ mm	$J=fRN'$	$=855$	$cN=88$
$aI=1000$	RN'	$=1710$	$N'=0.0002$
$dpN=2915$	$(1-f)RN'$	$=855$	$N=1.07$

With incident radiation supplied at the rate of 1000 quanta per sec., 1710 quanta are emitted by the vapor of which 855 escape as resonance radiation. There are 3060 collisions which result in the transition $^3P_1\rightarrow{}^3P_0$ and 2915 collisions in which the reverse process occurs. Hg_2' molecules are formed at the rate of 88 per sec. and 57 H_2 molecules, present as impurities, are dissociated. One five-thousandth of an atom represents the population of the $^3P_1$ level and one atom that of the $^3P_0$ level. Similar computations may be made for other pressures and for different admixed gases.

Attention should be directed to the fact that a normal Hg atom is effective in performing the transition $^3P_1\rightarrow{}^3P_0$; hence, if the present discussion were applied to experiments in which the Hg pressure were materially increased, the effect of such collisions should not be neglected. Also in considering the quenching due to Hg vapor alone, the variation of the absorption probability a with pressure becomes of great importance on account of the strong influence of coupled damping.

The writer desires to thank Dr. Gregory Breit of the Department of Terrestrial Magnetism for his helpful discussions during the preparation of this manuscript.

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WASHINGTON, D. C.

DEPOLARIZATION OF RESONANCE RADIATION*

By Paul D. Foote

Abstract

Depolarization and quenching of mercury resonance radiation are phenomena of quite different type. Depolarization is produced by two effects. With gases which quench by effecting the transition $^3P_1 \rightarrow {}^3P_0$ upon collision with Hg′ atoms, there exists a pronounced reverse transition $^3P_0 \rightarrow {}^3P_1$ produced by collision with high speed molecules. Atoms which radiate without any collision emit polarized light under the conditions of the experiment. Those which become $^3P_1$ atoms after having existed as $^3P_0$ atoms have experienced a large number of collisions and have lost their orientation relative to the incident electric vector; accordingly they emit radiation polarized in random directions. The second depolarizing influence arises in collisions at distances exceeding the ordinary kinetic theory collision such as is described above, at which the distance is too great for a collision of the first or second type, but still small enough for the field of the gas atom to exert a perturbing influence on the orientation of the Hg′ atom. Depolarization by H_2 is an excellent example of the second influence while the first effect is sufficient to interpret the experimental data with the rare gases, the atomic fields of which decrease with a high power of the radial distance.

ADMIXTURE of a foreign gas to a mercury resonance bulb decreases the intensity as well as the polarization of the emitted radiation. These two phenomena are frequently considered analogous whereas often they are more nearly of a reciprocal nature. A gas which is very effective in the destruction of polarization may have but small influence upon the intensity of the radiation. A gas might be effective as a quenching agent and either effective or ineffective for depolarization.

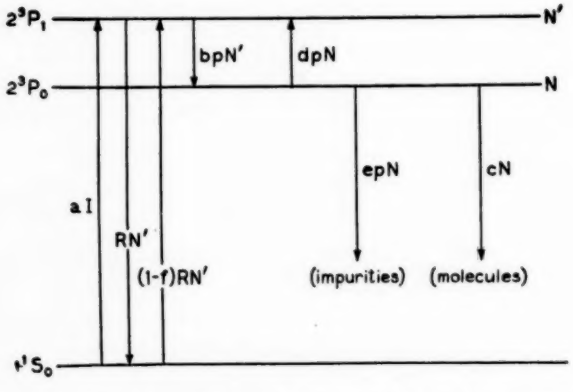

Fig. 1. Transitional diagram for Hg and rare gas mixture.

* Published with the approval of the Director of the Bureau of Standards of the U. S. Department of Commerce.

The quenching of resonance radiation by several gases has been discussed in a previous paper.[1] The cycle of transitions occurring with the rare gases and N_2 is represented by Fig. 1, the significance of the various processes and constants having been already considered in detail. The reason that the rare gases and N_2 are comparably ineffective in decreasing the intensity of the resonance radiation, $gJ=fRN'$, is due to the large number of transitions from $^3P_0$ to $^3P_1$ along dpN produced by collision of the metastable Hg′ atoms with high speed gas atoms. A large fraction of the quenching loss along bpN' is returned along dpN.

The same diagram applies in experiments on depolarization where the polarization of the radiation emitted in a direction perpendicular to the incident beam and to its electric vector is observed in the presence of a weak (or zero) magnetic field parallel to the electric vector. The Hg′ atom following absorption of the polarized quantum is oriented relative to the magnetic field and finally emits polarized radiation if undisturbed by collision. If a collision, in the sense of the kinetic theory, occurs, the $^3P_1$ atoms originally oriented by the radiation absorption become $^3P_0$ atoms. In this state they may suffer several hundred collisions with gas atoms, depending upon the pressure p until finally a large proportion of them collides with atoms which have energy sufficient to return them to the $^3P_1$ state. During this interval the orienting effect of the incident radiation has been lost[2] so that if atoms which have been subjected to this treatment eventually radiate, the polarization should be random.

Let J_1 = the intensity of radiation emitted by the atoms which emit immediately following absorption and J_2 = the intensity from atoms which have arrived to the $^3P_1$ state through the path dpN which has involved so many disturbing collisions. The intensity J_1 is polarized while J_2 is completely depolarized. From Fig. 1, and especially as discussed in the previous article, we have

$$\frac{aI}{dpN}=\frac{J_1}{J_2}=\left(1+\frac{c}{dp}+\frac{e}{d}\right)\left(1+\frac{Rf}{bp}\right)-1. \tag{1}$$

The customary definition of the percent polarization is

$$P=P_0/(1+J_2/J_1) \tag{2}$$

where $P_0=80$ = the percent polarization for zero pressure of the foreign gas and for very low pressure of the Hg vapor. The reason that $P_0=80$ instead of 100, as shown by MacNair, and Ellett[3] is due to the anomalous Zeeman pattern of one of the hyperfine structure components of λ2537, but this need not concern the present discussion.

Experiments on the polarization of resonance radiation are usually made with a quartz cell having two windows at right angles. The incident beam is directed on one face parallel and as close as possible to the second window

[1] Foote, this Journal, p. 288.

[2] For two reasons (a) collisions (b) inner quantum number is zero for the metastable state.

[3] McNair and Ellett, Proc. Nat. Acad. Sci., 1927.

(18°C), while the Hg pressure is controlled by a side tube cooled in an ice-salt mixture. The beam is sharply defined so at the low pressure $2 \cdot 10^{-5}$ mm, corresponding to -21°C, secondary resonance effects are negligible. The absorption coefficient of the vapor at this low pressure is small compared to that at room temperature, and the path for the emitted radiation is short. Hence, we are justified in putting the transmission factor $f=1$ in this type of experiment.

The constant c/d representing the ratio of the probabilities of a $^3P_0$ atom for forming a Hg_2' molecule and for colliding with a high speed gas atom is small even with a Hg pressure corresponding to room temperature. At Hg pressures of one hundredth this magnitude, the term c/dp may be neglected except when p is nearly zero. The term e/d is always small for a resonable impurity content and is negligible compared to unity. Substituting this approximate value of J_2/J_1 in Eq. (2) we obtain

$$P=P_0/(1+bp/R) \tag{3}$$

where b/R is a constant computed from kinetic theory. For argon $b/R=0.74$ and for He $b/R=1.42$ as derived in the earlier paper.

In this simple kinetic theory derivation we attribute the entire depolarizing influence of the foreign gas to the random emissions following the $^3P_0 \rightarrow {}^3P_1$ transitions by collision. In general, however, there is another effect operative. As in the quenching of resonance radiation, we are justified in assuming that an effective collision occurs every time two molecules approach within a distance equal to the sum of their kinetic theory radii. At such a collision between Hg′ and a gas molecule there is an energy exchange of some form, either a collision of the first or second type. But in addition there must be collisions in which the approach is not close enough to effect a transfer between the $^3P_1$ and $^3P_0$ levels, "disturbing" collisions in which the orientation of the Hg′ atom is perturbed by the field of the foreign gas atom. Such perturbation results in a depolarizing influence upon the emission. This effect should be a minimum for the rare gases which present a closed electronic structure for which the electric field decreases with a high power of the radial distance. Hence, Eq. (3) might be expected to satisfy approximately the experimental data for depolarization by rare gases. In Fig. 2 the full lines are drawn in accordance with Eq. (3) while the plotted points are the experimental values for A and He as determined by von Keussler.[4] The qualitative agreement confirms the above assumption that for atoms with small stray fields the depolarization is mainly due to the emission of random polarization following the transition $^3P_0 \rightarrow {}^3P_1$, the latter having been effected by collision with high speed atoms in accordance with ordinary kinetic theory.

According to Eq. (3) the half-value of the polarization occurs at $p=R/b$. For N_2, $R/b=1.12$ mm whereas von Keussler observed $p=0.51$. The depolarization is therefore more rapid than can be accounted for by the $^3P_0 \rightarrow {}^3P_1$ transitions so that the field from a N_2 molecule must have a dis-

[4] von Keussler, Ann. d. Phys. **82**, p. 828 (1927).

turbing action on the orientation of the Hg′ atom. It is quite possible that by increasing the strength of the magnetic field, parallel to the exciting electric vector, the perturbing action of the atomic field could be suppressed.

Foreign gases which have a work of dissociation or critical potential in the range corresponding to the energy of the excited Hg′ atom may quench the excited state directly. For example, with H_2 alone the population of the $^3P_0$ level is always approximately zero. The transitions bpN' and dpN do not occur in an appreciable degree. After a kinetic theory collision, therefore, the life history of the particular Hg′ atom is temporarily complete. It emits no radiation to be depolarized. Hence, all of the depolarization produced by H_2 is due to collisions of the perturbing type at some distance of approach for the two atoms which exceeds the sum of their kinetic theory radii. We may roughly estimate this distance.

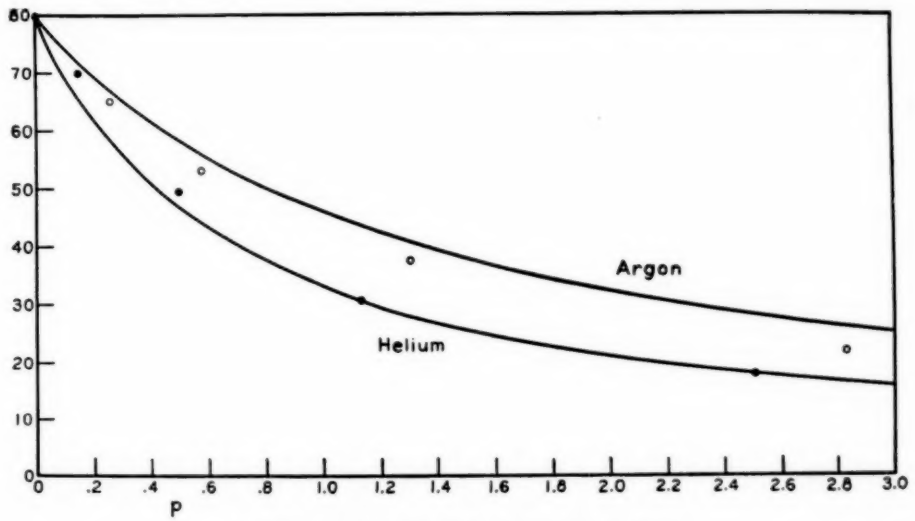

Fig. 2. Depolarization by argon and helium.

Suppose that the approach of the H_2 molecule produces a random orientation of the Hg′ atom. This is an extreme view which will yield a minimum value for the collision distance. Let ρ be this collision distance while σ = the effective quenching distance (sum of the kinetic theory radii). Collisions for distances lying between ρ and σ produce depolarization. From kinetic theory this collision rate is given by

$$\nu_2-\nu_1=2.61\cdot 10^{22}(\rho^2-\sigma^2)p\left(\frac{M_1+M_2}{M_1M_2}\right)^{1/2} \tag{4}$$

At some pressure p there is equal probability for the Hg′ atom to radiate or to suffer a perturbing collision. At this pressure the polarization is, according to Eq. (2), reduced to half-value. The time between such collisions is equal to the life of the $^3P_1$ atom in the undisturbed state or $\nu_2-\nu_1=1/\tau=9.1\cdot 10^6$. Substituting this and the pressure, $p=1.54$ mm, observed by von Keussler,

which is used for observation. The cell is operated at room temperature in Eq. (4) we find $\rho^2-\sigma^2=3.2\cdot10^{-16}$. The distance σ = the sum of the quenching radii, $2.03\cdot10^{-8}$ cm for Hg′ and $1.34\cdot10^{-8}$ cm for H_2. Hence, $\rho=3.8\cdot10^{-8}$ cm. On this extreme assumption nothing happens until the H_2 molecule approaches within $3.8\cdot10^{-8}$ cm of the Hg′ atom. If the H_2 molecule approaches within the distance $3.8\cdot10^{-8}$ to $3.3\cdot10^{-8}$, the orientation of the Hg′ atom is given a random direction. If the collision be closer than $3.3\cdot10^{-8}$ cm, the H_2 molecule is dissociated and no radiation is emitted.

With gases such as O_2, CO, CO_2, H_2O, the phenomena are probably more complicated. Apparently certain of these may quench by absorption of the energy, analogous to the effect with H_2, and also by collision resulting in the $^3P_1\rightarrow{}^3P_0$ transition. The depolarization, as with N_2, then should be due to the two different effects described above.

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THEORY OF NORMAL CATHODE FALL IN GLOW DISCHARGES

By K. T. Compton and P. M. Morse

Abstract

Basis of theory of cathode fall.—From the principle of minimum energy dissipation it is shown that the actual potential distribution in the fall space must be that one which is most favorable to ionization, subject to limitations imposed by Poisson's equation. With the aid of this principle, taking as known quantities the normal cathode fall V_n and Townsend's ionization constants N and V_0, expressions are derived for the *potential distribution*, the *thickness of the fall space* d_n, the *distribution of ionization* n_x and the *current density* j_n which agree acceptably with experimental values.

Results of theory.—The most important results are given by the equations

$$pd_n = 0.85\frac{V_n}{NV_0}\left(1+\frac{V_0}{0.97V_n}+\cdots\right)$$

$$\frac{j_n}{p^2} = 1.85(10)^{-4}\left(\frac{L}{M}\right)^{1/2}\frac{(kN)^{3/2}V_n^{3/2}}{(1-n_0/n_d)},$$

in which L, M and p are molecular mean free path, molecular weight of positive ions and gas pressure.

Explanation of normal and abnormal cathode falls.—It appears that the normal cathode fall is found when the potential is distributed in the manner most favorable to ionization, without restriction by space charge considerations. When the current density exceeds the normal value, space charge considerations require a less favorable potential distribution and hence a larger cathode fall,—which is the *abnormal* case.

Introduction

GREAT difficulties have been encountered in attempts to develop a theory of the cathode fall in glow discharges. These difficulties are twofold; very general physical assumptions lead to insuperable mathematical difficulties and we are prevented, by lack of knowledge of the exact character of processes involved, from making more specific assumptions which seem reasonable and adequate. Of several theories of the cathode fall, the most satisfactory have been those of H. A. Wilson,[1] Ryde[2] and Güntherschulze.[3]

The empirical relations and data which must be satisfied by a successful theory are, principally, the following: (1) When the current is so small that the cathode is only partially covered with glow ("normal" case), the cathode fall of potential has a constant minimum value V_n which is characteristic of the gas and the material of the cathode. (2) Associated with the normal cathode fall is a normal current density j_n which depends on the nature and pressure of the gas and the material of the cathode. (3) The thickness d_n of the normal cathode fall space depends on the nature and pressure of the

[1] H. A. Wilson, Phys. Rev. **8**, 227 (1916).
[2] Ryde, Phil. Mag. **45**, 1149 (1923).
[3] Güntherschulze, Zeits. f. Physik. **33**, 810 (1925).

gas. (4) If the total current exceeds the value at which the glow just covers the cathode we have the *abnormal* cathode fall, in which $V_a > V_n$, $d_a < d_n$, $j_a > j_n$. (5) Empirical quantitative relationships between these quantities are as follows:

$$pd_n = A, \tag{I}$$

$$j_n/p^2 = B, \tag{II}$$

where A and B are constants for any given gas and cathode material. The potential distribution in the normal cathode fall space is unknown. In the abnormal fall space Aston[4] found the field strength E to be proportional to the distance $(d-x)$ into the fall space from the anode side, or

$$E \propto (d-x). \tag{III}$$

Examination of the Stark effect on spectral lines from this region, however, leads to a somewhat different conclusion,[5] also in the case of the abnormal cathode fall.

H. A. Wilson's theory[1] is the most general and comprehensive one yet attempted. It assumes ionization by collisions of electrons and positive ions with molecules in the fall space, taking Townsend's quantities α and β as the measure of this ionization; it allows for electron emission from the cathode under positive ion bombardment; it takes the potential distribution to be governed by Poisson's equation; it considers the mobilities of the electrons and ions to be constant, *i.e.*, their rates of advance to be proportional to the field (with a correction due to the variation of the field from point to point). This last assumption is the weak point of the theory, since it is now well known that the mobility is a function of the field.[6] The theory gives relations (I) and (II) above but does not give quantitative values.

Ryde[2] and Güntherschulze[3] almost simultaneously proposed a theory which assumes that the space charge in the fall space is due entirely to positive ions and that these pass unhindered by collisions through the fall space, as if in a vacuum discharge between parallel electrodes. Then Eq. (IV), the familiar space charge equation of Child[7] and Langmuir[8] holds.

$$j_+ = \frac{(2)^{1/2}}{9\pi}\left(\frac{e}{M}\right)^{1/2}\frac{V^{3/2}}{d^2} \tag{IV}$$

According to this, relation (II) is satisfied if (I) be assumed, and the values of j calculated by substitution of experimental values of V and d come out of the right order of magnitude. But the field distribution is not even approximately like (III), since Eq. (IV) leads to $E \propto (d-x)^{1/3}$. Furthermore the theory fails to give relation (I). From a physical standpoint the theory

[4] Aston, Proc. Roy. Soc. A., **84,** 526 (1911).
[5] Brose, Ann. d. Physik. **58,** 731 (1919).
[6] Loeb, Phys. Rev. **19,** 24 (1922); Compton, *ibid.*, **22,** 333, 432 (1923).
[7] Child, Phys. Rev. **32,** 492 (1911).
[8] Langmuir, Phys. Rev. **2,** 450 (1913).

is particularly unsatisfactory in two respects. The assumption of free motion of positive ions through the fall space is incompatible with the fact that the fall space is of the order of 100 free paths in thickness. (In this respect Ryde, who applies his theory only to the abnormal case, where $d_a < d_n$, is more defensible than Güntherschulze.) The assumption that positive ions move freely through the fall space implies that electrons, with their longer free paths, do likewise, which would put all the ionization by electron impacts in the nearly field free negative glow with no opportunity for the ionization to increase exponentially. Under such conditions Lehman[9] has found that the total number of new ion pairs would lie between $V_n/3V_i$ and $3V_n/4V_i$, depending on the nature of the gas. Not all of the positive ions so formed would reach the cathode, owing to loss by recombination and diffusion to the walls. Hence, to maintain the discharge, a very improbably large electron emission from the cathode under positive ion bombardment would be required; in nitrogen, for instance, more than one electron for every five impinging positive ions would be required.

In the following treatment of this problem we have avoided (except in one phase of the subject) the uncertainties introduced by the use of electron and ion mobilities and assumptions regarding the probabilities of ionization or electron emission from the cathode, and have based the treatment on a minimum number of directly observed quantities and on a general principle which does not seem previously to have been used in the theory of conduction through gases.

General Statement of Theory

Consider the condition of a gas when it carries current i. There is an infinite variety to the ways in which potential *might* be distributed so as to permit this flow of current, but of all these ways there is some one distribution which is distinguished by the fact that it is the most favorable for the passage of this particular current, so that the potential drop V required to produce the current is less, with this particular distribution, than with any other. This most favorable distribution is the actual distribution, since it permits the passage of the current with the minimum dissipation of energy. We shall, therefore, employ the principle that *the actual potential distribution is that which is most favorable to the passage of current, subject to the limitations imposed by Poisson's equation.*

The application of this principle to the cathode fall is particularly simple since here, if anywhere, the complicating effects of recombination and diffusion are negligible in comparison with other factors which can at least approximately be evaluated. The most favorable distribution of potential is that for which an electron, after leaving the cathode, produces the maximum ionization as the result of its passage through the fall space.

In order to calculate the ionization we use Townsend's equation

$$\alpha = pN\epsilon^{-pNV_0/E} \tag{1}$$

[9] Lehman, in print.

which is known accurately to give the number of ionizing collisions made by an electron in 1 cm of advance in a field E in terms of two constants, N and V_0, characteristic of the gas. To what extent this equation is empirical and to what extent it has a theoretical basis need not concern us here. We are interested only in the fact that it is so accurate that no appreciable deviations from experiment have been found except in the case of helium, and even in this case the error is not large.[10]

We shall take as known quantities Townsend's constants N and V_0 and also the value of the normal cathode fall V_n, which is the most accurately known quantity pertaining to the cathode fall. The considerations which, in turn, determine V_n will be discussed later. From these three quantities, and the principle enunciated above, we shall derive relations (I) and (II) with fair quantitative accuracy, a reasonable law of variation of E with x, and an explanation also of the abnormal cathode fall.

Potential Distribution

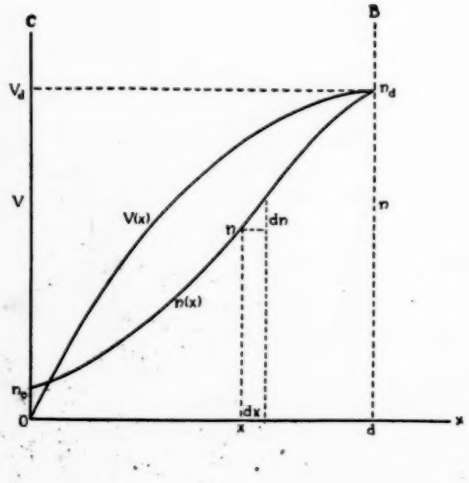


Fig. 1.

Let $V=V(x)$ be the law of distribution of potential between the cathode C and the outer boundary B of the cathode fall space, whose distance d from the cathode is still to be determined. Corresponding to the potential distribution $V(x)$ is a field distribution $E=E(x)=-V'(x)$. Through some agency (which need not here concern us) let n_0 electrons be emitted from the cathode. At distance x this number has increased, through ionization of the gas, to n. In the ensuing distance dx the increase is $dn=n\alpha dx$. Thus the total number of electrons emerging from the fall space is

$$n_d=n_0\epsilon^{\int_0^d \alpha dx} \tag{2}$$

As explained above, we are to choose $E(x)$ and d so as to lead to a maximum value of n_d. This maximization is expressed by

$$\delta\int_0^d \alpha dx=\delta\int_0^d pN\epsilon^{-pNV_0/E(x)}dx=0, \tag{3}$$

subject to

$$-\int_0^d E(x)dx=V_n. \tag{4}$$

[10] Townsend, "Electricity in Gases," Chap. VIII; Compton, Phys. Rev. 7, 501, 509 (1916).

We must note, however, that Eq. (1) gives α only when the field E is uniform, so that correction must be made in the present case for the effect of non-uniformity of field. A first order correction may be made as follows:

Townsend originally interpreted pN as the number of collisions made per unit path by an electron and V_0 as the minimum ionizing potential of the gas. He assumed that all impacts were completely inelastic and that all impacts with energy greater than V_0 resulted in ionization. We know that these assumptions are untrue. However, the equation (1) derived from these assumptions agrees so well with experiment (with properly chosen values of N and V_0) that we should be justified in using the same assumptions for the purpose of estimating the relatively small correction required to allow for non-uniformity of the field, which we proceed to do.

An electron which collides at a point x where the field is E has come, on the average, from its last collision at a point $x-l$, where l is the mean free path $l=1/pN$. The electron therefore has come from a region where the field is $E-(1/pN)\,E'$, and its energy when it collides at x is characteristic of the mean field $E-(1/2pN)\,E'$. This, rather than $E(x)$, should be used in Eq. (3), so that we have to determine d and $E(x)$ from Eq. (4) and

$$\delta\int_0^d pN\,\exp\left[-\frac{pNV_0}{E-E'/2pN}\right]dx=0 \tag{5}$$

When $E(x)$ and d are thus found, we can calculate the total "multiplication factor" n_d/n_0 from

$$\log\frac{n_d}{n_0}=\int_0^d pN\,\exp\left[-\frac{pNV_0}{E-E'/2pN}\right]dx. \tag{6}$$

The problem could be carried on from this point through use of Eq. (6) alone, by the process of substituting a number of assumed forms of $E=E(x)$, maximizing in each case with respect to d, and selecting that form of $E(x)$ and value of d which give the maximum multiplication factor as being at least approximately correct. This we did at first, but later succeeded in solving Eq. (5) by the following method of the calculus of variations.

Write, for the number of electrons crossing a plane x,

$$\log\frac{n_x}{n_0}=pN\int_0^x\exp\left[-\frac{pNV_0}{E-E'/2pN}\right]dx=pN\int_0^x\epsilon^\nu dx=pN\int_0^x\phi(E,E')dx. \tag{7}$$

To obtain a function $E=E(x)$ such that $\int_0^x\phi(E,E')dx$ is maximum, we must solve the differential equation

$$\frac{d}{dx}\left(\frac{\partial\phi}{\partial E'}\right)=\frac{\partial\phi}{\partial E}, \tag{8}$$

where

$$\frac{\partial\phi}{\partial E'}=-\frac{V_0\epsilon^\nu}{2(E-E'/2pN)^2}\text{ and }\frac{\partial\phi}{\partial E}=+\frac{pNV_0\epsilon^\nu}{(E-E'/2pN)^2} \tag{9}$$

With these substitutions Eq. (8) becomes

$$2EE' - pNV_0E'/2 + V_0E''/4 - EE''/2pN + E'E''/4p^2N^2 - pNE^2 - 3E'^2/4pN = 0$$

which has a particular solution

$$E = kpNV_L\epsilon^{-kpNx} \tag{10}$$

$$V = -\int_0^x E\,dx = V_L - V_L\epsilon^{-kpNx} \tag{11}$$

in which k and V_L are constants of integration. We thus have, from Eq. (7),

$$\log(n_x/n_0) = pN\int_0^x \epsilon^{-A\epsilon^z}dx = (1/k)\left[z - J(A\epsilon^z) + J(A)\right], \tag{12}$$

where

$$z = kpNx,\quad A = \frac{V_0}{V_Lk(1+k/2)},\quad J(y) = y - \frac{y^2}{4} + \frac{y^3}{18} - \frac{y^4}{96} + \cdots. \tag{13}$$

Next we must choose the constant k so as to maximize the multiplication factor, which can be done by solving

$$\frac{d}{dk}\left(\log\frac{n_d}{n_0}\right) = \frac{d}{dk}\left(pN\int_0^d \epsilon^{-A\epsilon^z}dx\right) = 0,\ \text{or}$$

$$\frac{1+k}{1+k/2}(\epsilon^{-A} - \epsilon^{-A\epsilon^{z_d}}) + z_d\epsilon^{-A\epsilon^{z_d}} - z_d + J(A\epsilon^{z_d}) - J(A) = 0,$$

where $z_d = kpNd$ is the value of z when $x = d$, at the outer boundary of the cathode fall space. A comparison of Eq. (10) with empirical expressions for $E(x)$ which are found by substitution in Eq. (6) to give close to the maximum value of n_d/n_0, shows that k is considerably less and z_d is larger than unity in the case of every gas. Thus to a very close approximation the fraction $(1+k)/(1+k/2)$ may be taken as unity, and our equation reduces to

$$z_d - \epsilon^{-A} - (z_d - 1)\epsilon^{-A\epsilon^{z_d}} = J(A\epsilon^{z_d}) - J(A). \tag{14}$$

It is found that the solution $A = 0.40$ satisfies this equation very closely, whatever value of z_d larger than about 2 be assumed. Thus we have a definite relation between the constants k and V_L given by

$$A = \frac{V_0}{V_Lk(1+k/2)} = 0.40 \tag{15}$$

From this, solving for k and expanding, we find

$$k = \frac{V_0}{0.4V_L} - \frac{V_0^2}{0.32V_L^2} + \cdots \tag{16}$$

In order to find the thickness d_n of the fall space, we must adopt a method of defining its outer boundary. We have arbitrarily chosen this as the point at which the slope of the curve of log (n_x/n_0) against z becomes $1/10\ k$. This gives the boundary shown by the vertical dashed line in Figs. 2–5 and is seen to give practically the ultimate value of n_x/n_0. Just in this region the analysis is not rigid, since here alone the effect of initial velocities of ions and of diffusion is appreciable in comparison with effects of the field which alone we are considering. In any case this choice of the limit d_n cannot be far from correct. It is, for example, close to the value which would be selected by taking the intersection of two straight lines drawn tangent to the (n_x/n_0) vs pd curve at the nearly straight regions on either side of the sharp bend near the top of the curve. With this definition,

$$\frac{d}{dz}\left(\log\frac{n_x}{n_0}\right)=\frac{d}{dz}\left(pN\int_0^x \epsilon^{-Ae^z}dx\right)=\frac{1}{10k},$$

whence

$$\epsilon^{-Ae^{z_d}}=1/10,\ \text{or}\ z_d=\ln(2.3/A)=1.75 \tag{17}$$

is a constant for all gases.

Now a closer approximation may be made by using this value of z_d in Eq. (14) to redetermine A, then recalculating z_d, again recalculating A, etc. When this is done, the values do not differ appreciably from those here given.

It remains to determine the constant V_L. This is done by noting that, at $x=d_n$, $V=V_n$, which is one of our given quantities. From Eqs. (11) and (17) this gives

$$V_L=V_n/(1-\epsilon^{-z_d})=1.21V_n \tag{18}$$

Finally, from Eqs. (11), (17) and (18) we obtain

$$V=1.21V_n(1-\epsilon^{-1.75px/pd_n}) \tag{19}$$

$$pd_n=0.85\frac{V_n}{NV_0}\left(1+\frac{V_0}{0.97V_n}+\cdots\right) \tag{20}$$

Eq. (20) conforms to the empirical law (I) and permits theoretical calculation of pd_n in terms of the constants N, V_0, V_n. The values for several cases are shown in Table I.

TABLE I

Values of the constants N, V_0, V_n. The pressure, p, in mm Hg; *d is in cm; iron cathode.*

Gas	N	V_0 (volts)	V_n (volts)	pd_n (calc)	pd_n (obs)
N_2	12.4	27.6	253	0.77	0.419
A	13.6	17.3	165	0.66	0.356
H_2	5.0	26.0	270	1.81	0.900
He	2.8	12.3	160	4.25	1.660

Townsend's values[10] are used for N and V_0, while Güntherschulze's values[11] are taken for the cathode fall with an iron cathode in the various gases. In comparing the observed with the calculated values, several facts must be kept in mind. Most important is the fact that the only available observed values of pd_n are for cases in which d_n refers to the thickness of the Crooke's dark space, measured as the distance between the cathode and the more or less sharp edge of the negative glow. This edge is defined by the psychological interpretation of a physiological effect on the eye and is found to be the region in which the light intensity varies most rapidly with respect to distance from the cathode and to be about half the distance to the point at which the light reaches maximum intensity.[12] This latter, rather than the visual distance, would most probably correspond to the distance d_n of our calculations. In any case, our d_n is defined as the distance within which the cathode fall of potential occurs and should be measured to the region at which the field falls to a minimum value. Such measurements have not been made with sufficient accuracy and in enough cases to permit their use but they have shown that the fall space as thus electrically defined is considerably greater in thickness than the visually estimated dark space.[13] Thus our calculated values are (except in the case of helium) perhaps within the range of possibility, and are certainly at least close to the correct values.

Furthermore, measured values of N, V_0, V_n and d_n all depend greatly on the degree of purity of the gases used. Since these data come from three independent sets of investigations, some of rather old date, good agreement would scarcely be expected. It is highly desirable to make all the necessary measurements involved in a test of Eq. (20) on the same sample of gas, under identical conditions, and to measure d_n electrically rather than visually. Such work is now being undertaken in this laboratory.

Finally it should be remarked that Townsend's equation (1) is less accurate in the case of helium than in the other gases,[10] so that anything better than order of magnitude agreement with experiment is not to be expected in the case of this gas.

TABLE II

Values of pd_n for Fe and Al cathodes from Guntherschulze[14]

Gas	N_2	A	H_2	He	Ne	O_2	Mean
pd_n (Fe)	.419	.356	.900	1.66	.722	.311	
pd_n (Al)	.305	.285	.724	1.32	.637	.237	
Ratio (obs)	1.37	1.25	1.24	1.26	1.14	1.31	1.26
Ratio (calc)	1.16	1.32	1.30	1.33	1.28	1.12	1.25

Another prediction of Eq. (20) is that, for any given gas, the value of pd_n should vary with the cathode material, being nearly proportional to V_n. The rather meager and erratic data which are available[14] support this

[11] Güntherschulze, Zeits. f. Physik. **23,** 336; **28,** 129; **30,** 175 (1924).

[12] Seeliger and Lindow, Phys. Zeits. **26,** 393 (1923).

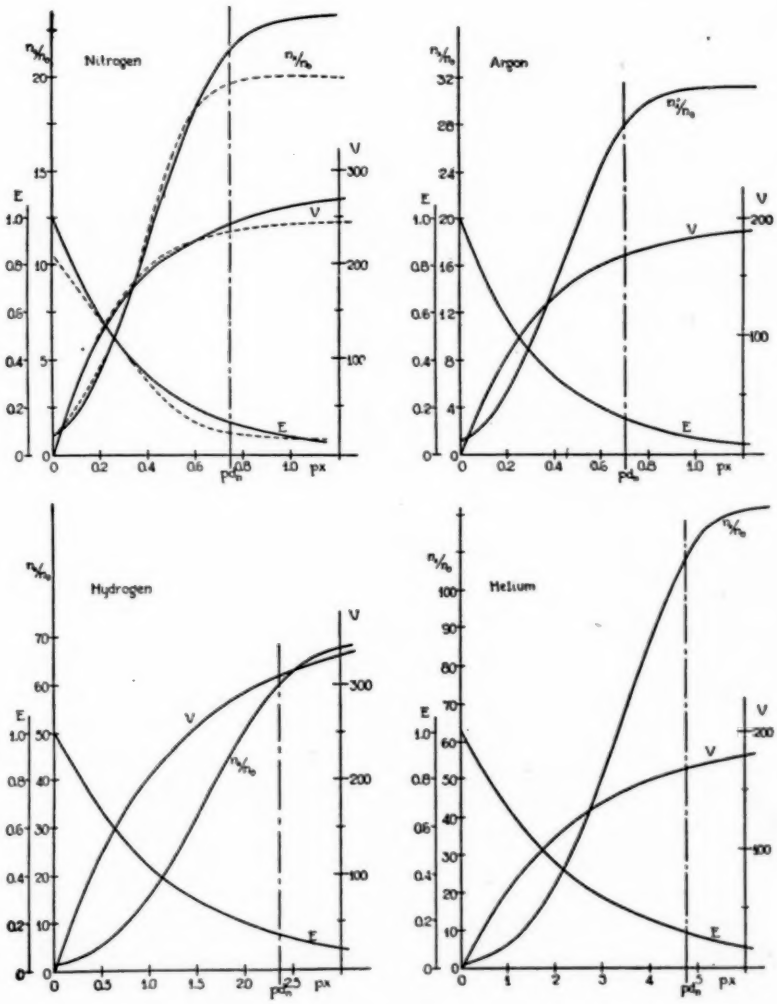
[13] Bär, Handbuch der Physik (Springer) XIV, p. 200.

[14] Bär, Handbuch der Physik (Springer) XIV, pp. 190, 191.

conclusion, as shown in Table II. Here the values used for V_n are the means of those found by numerous investigators.[15]

Distribution of Ionization

Eq. (12), with the definitions and values given by Eqs. (13), (15) and (16), permits the calculation of the multiplication factor n_x/n_0 at any distance x from the cathode. In Figs. 2–5 are shown these values calculated



Figs. 2, 3, 4, 5.

for N_2, A, H_2 and He, using values of V_n for *platinum* cathodes.[15] In all these figures it is only the part to the left of the vertical pd_n line that is significant, the part to the right being simply an extrapolation according to the equations.

[15] Bär, Handbuch der Physik (Springer) XIV, p. 203.

At the boundary $x=d_n$ all the current is carried by electrons. At the cathode $x=0$, however, n_d-n_0 positive ions enter and n_0 electrons leave. Similarly, at any intermediate point x the fraction $(n_d-n_x)/n_d$ of the total current is carried by positive ions.

Current Density

Except very close to the boundary of the cathode fall space, at $x=d_n$, we are justified in neglecting the contribution of the electrons to the space charge, in comparison with that of the positive ions. This is because the velocity of advance of the electrons is several hundred times that of the positive ions, their relative speeds being greater than the inverse ratio of the square roots of their masses by a factor which depends on the collision frequency and type. This difference is further enhanced by the fact that the electrons crossing any plane have come from a region of larger field strength than the positive ions which cross the same plane in the opposite direction. We shall therefore apply Poisson's equation to the space charge arising from the positive ions.

Let j_n be the total normal current density, and j_x^+ the positive ion current density at the point x. Then

$$j_x^+/j_n=1-n_x/n_d. \tag{21}$$

By Poisson's equation we have

$$-dE/dx=4\pi\rho=4\pi j_x^+/\bar{v}=4\pi j_n(1-n_x/n_d)/\bar{v}, \tag{22}$$

in which the negative sign of the first member appears because we have taken the positive direction of x opposite to that of E. $\bar{v}$ is the average velocity of advance of the positive ions. In the absence of either experimental or satisfactory theoretical knowledge of $\bar{v}$, we have estimated it according to the simplest classical theory in the following manner.

If the ions and molecules be treated as spheres of equal mass, direct application of the energy and momentum principles leads to the conclusion that the mean energy loss by an ion at a collision is half the energy before impact, and that the average deflection is through an angle of 45°.[16] If W is the average energy gained from the field during one free path, it is readily seen that the energy of an ion just before its nth collision (after starting from rest) is $(2^n-1)W/(2^{n-1})$, while just after the nth collision it is $(2^n-1)W/2^n$. Thus we see that a terminal state is very quickly approached in which the energy at the beginning of a free path is W and that at the end is $2\ W$ If v_0 is the velocity corresponding to kinetic energy W, the mean velocity during the free path is $\bar{v}=(1+2^{1/2})\ v_0/2=1.2\ v_0$.

Now W cannot exceed $E\ e\ l$, where l is the ionic mean free path, since it would have this value only if the ions moved through the gas without sidewise deflection. This upper limit gives $\bar{v}=1.2(2\ E\ e\ l/M)^{1/2}$, where M is the molecular weight of the ion. On the other hand the average inclination of the path to the direction of the field cannot exceed 45°, whence a

[16] Similar to the calculation by Compton, Phys. Rev. **22**, 333 (1923).

lower limit is $\bar{v}=1.2/2^{1/2}(2\ E\ e\ l/(2)^{1/2}M)^{1/2}$. We cannot be in error by as much as 20 percent if we take the mean of these two limits, or

$$\bar{v}=.96(2Eel/M)^{1/2}. \tag{23}$$

If we substitute this for $\bar{v}$ in Eq. (22), and also substitute for E from Eq. (10), we obtain

$$j_n=(.96/4\pi)(2el/M)^{1/2}(kNp)^{5/2}V_L{}^{3/2}\epsilon^{-3/2kpNx}/(1-n_x/n_d).$$

But the ionic free path l may be taken as $2^{1/2}$ times the molecular free path, since the ions are moving rapidly as compared with the molecules. Calling L the molecular free path at 1 mm pressure, we may put $l=2^{1/2}L/p$. We may also substitute for V_L its equivalent 1.21 V_n, by Eq. (18). With these substitutions, and with reduction of the numerical factors, the equation becomes

$$j_n/p^2=0.17(eL/M)^{1/2}(kN)^{5/2}V_n{}^{3/2}\epsilon^{-3/2kpNx}/(1-n_x/n_d).$$

If, as is customary, we express j_n in milliamperes per cm², V_n in volts and M in ordinary units of molecular weight, and also substitute numerical values for the constant e/M_H, and rewrite the exponential factor with the aid of Eq. (17), we obtain

$$\frac{j_n}{p^2}=1.85(10)^{-4}\left(\frac{L}{M}\right)^{1/2}\frac{(kN)^{5/2}V_n{}^{3/2}}{(1-n_x/n_d)}\epsilon^{-2.64px/pd_n}\frac{\text{m.a.}}{\text{cm}^2\text{mm}^2} \tag{24}$$

Since k is given in terms of the constants V_0 and V_n by Eqs. (16, 18), we are able to calculate j_n by using the value of n_x/n_d calculated by Eq. (12) for any value of px.

It is most convenient to calculate j_n/p^2 at $x=0$, $n_x=n_0$. In so doing the chief uncertainty is regarding the temperature of the gas, which is involved in obtaining the molecular mean free path L at 1 mm pressure. Here the experimental evidence is very inadequate, but from some work by Seeliger,[17] together with the fact that more energy is liberated in the fall space than elsewhere, we shall probably not be far wrong if we take the temperature to be 273°C. While this may be incorrect, it is scarcely conceivable that the error can exceed 25 percent, since the square root of the temperature is involved. In this way Eq. (24) leads to the values in Table III.

TABLE III

j_n in milliamps/cm²; p in mm; V_n for Pt cathode.

Gas	N_2	A	H_2	He
V_n	232	162	300	165
n_d/n_0	21.5	27.9	62.0	109
$(j_n)^{1/2}/p$ (calc)	0.420	0.294	0.245	0.188
$(j_n)^{1/2}/p$ (obs) I	0.576	0.346	0.320	0.097
$(j_n)^{1/2}/p$ (obs) II	<.501	<.301	<.278	<.085

[17] Seeliger, Phys. Zeits. **27**, 732 (1926).

The best observations of normal current density seem to be those of Güntherschulze,[18] who operated with platinum cylinders of different radii and at different gas pressures and took the values obtained with the cylinder of largest radius (6.33 mm) and largest gas pressure (about 4 mm) as most nearly approximating the values for a plane cathode. These values are given in row (obs) I. His other work in hydrogen, however, shows that the values with the cylindrical cathode are larger than those for a plane cathode. Taking the mean correction factor from these measurements and applying it to all four gases, we obtain values shown in row (obs) II. The true values should be slightly smaller than these, owing to differences in the temperatures reached by cylindrical and plane cathodes, but the exact amount of this correction is unknown. Here again the calculated values are certainly within the range of probable experimental values (except again in the case of helium), as far as we can tell in view of the uncertainties involved in the calculations.

Limits Imposed by Poisson's Equation

In calculating the multiplication factor n_x/n_0 by Eq. (12) no account was taken of any possible limitation imposed by Poisson's equation, the values being obtained by assuming a potential distribution to give maximum ionization, without inquiring whether this distribution was possible in view of space charge considerations. We are now in a position to make this inquiry.

The normal current density j_n is of course constant at all values of x within the fall space. We may therefore take j_n/p^2 as calculated above and use Eq. (24) to give n_x/n_d, from which n_x/n_0 is at once found. If these values agree with those previously calculated, it means that our treatment is consistent with the requirements of Poisson's equation.

In Fig. 2 the dotted curves show the values of n_x/n_0, V and E (this last subject to an arbitrary additive constant) which are exactly consistent with Poisson's equations. The agreement is seen to be nearly perfect practically up to $x=d_n$, beyond which the curves have no physical significance and near which our treatment, as we have pointed out, is inadequate.

Discussion

Since this theory, without adjustable constants, leads quantitatively to the laws of the normal cathode fall and satisfies, as accurately as could be expected, the experimental tests which we are in a position to make on it, we believe that the idea underlying it is correct. The most significant conclusion appears to be this: *The normal cathode fall is distinguished by that distribution of potential which is most favorable to ionization, unrestricted by limitations imposed by Poisson's equation.* If the current density were increased above the normal value j_n, it is obvious that the same potential distribution could not exist, but a less favorable one would be required by Poisson's equation;—necessitating an increased cathode fall in order to

[18] Güntherschulze, Zeits. f. Physik. **20**, 1 (1923); Bär, Handbuch der Physik (Springer) XIV, pp. 211, 212.

supply the larger current density despite the less favorable potential distribution. *The principle of minimum energy dissipation therefore requires the normal current density j_n characteristic of the most favorable potential distribution so long as the total current does not exceed j_n times the area of the cathode: if the total current exceeds this value, we have the abnormal cathode fall characterized by $j_a > j_n$, $V_a > V_n$, $d_a < d_n$.*

The total multiplication factor n_d/n_0, shown in Table III, is interesting because it is so small. In order that the discharge may be self-maintained, it is necessary that, on the average, one electron should be liberated from the cathode (by positive ion bombardment, photoelectric effect, etc.) for every $(n_d - n_0)/n_0$ positive ions which are formed in the fall space. Evidence is decisive that such large emission from positive ion bombardment cannot occur from well degassed electrodes in good vacua,[19] and ordinary photoelectric effect is certainly too small. However the presence of the gas, with possibly adsorbed gas layers and certainly with a layer of excited and recombining ions, may quite possibly account for emission as large as that here demanded. There is at present no certain experimental evidence on this point.

Finally, a word should be said in regard to factors which determine the normal cathode fall V_n. We can only say that this is determined by that emissivity of electrons from the cathode and multiplication of ions in the fall space which combine to permit a self-maintained discharge at a minimum cathode fall. Large electron emissivity and easy gas ionization favor this condition at low values of cathode fall. Not enough is known regarding the mechanism of this emission to make it possible to incorporate this aspect fo the problem in our theory at the present time.

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PRINCETON, NEW JERSEY.
June 6, 1927.

[19] Jackson, Phys. Rev. **28**, 524 (1926).

HEATS OF CONDENSATION OF ELECTRONS AND POSITIVE IONS ON MOLYBDENUM IN GAS DISCHARGES

By C. C. Van Voorhis

Abstract

New method for measuring the electronic work function.—A new calorimetric method for measuring the electronic work function of a metal in a gas discharge, has been developed. A small molybdenum sphere was supported in a region of intense gas ionization by three fine wires, two of which formed a thermocouple to measure its temperature, while the third carried the current of the incoming ions. Space potential and mean electronic energies E_- were found by using the sphere as a Langmuir collector. Its rate of heating due to an increment Δj in the electron current reaching it against a small retarding field was measured and equated (with small corrections) to $\Delta j(E_-+\phi_-)$, whence the heat of electron condensation ϕ_- was found.

Values of ϕ_- for molybdenum in argon, hydrogen and nitrogen.—The values of ϕ_- found by this method were: 4.76 volts in argon, 4.04 or 4.35 volts in hydrogen (mixed with argon), and 4.77 or 5.01 volts in nitrogen. The double values follow different treatments of the surface. Owing to uncertainty in the specific heat values of molybdenum these results may be a few percent too high, consequently all the information required for making any necessary corrections from more satisfactory specific heat values has been given.

Measurement and theory of the heating effect on molybdenum due to the neutralization of an argon positive ion at its surface.—By a modification of the method, ϕ_+ for an argon positive ion neutralized at a molybdenum cathode was found to be about one volt. This low value indicates that a large part of the energy of neutralization at the cathode of a discharge tube is lost by the neutralized molecules, probably by radiation, before they make thermal contact with the metal.

Confirmatory evidence for "secondary" electrons.—The presence in a low pressure gas discharge, of the high speed "secondary" electrons discussed by Langmuir, is shown by the good agreement between values of E_- obtained calorimetrically and values calculated from the log j - against-voltage lines of the two groups of electrons, as obtained by Langmuir's methods.

IN RECENT years numerous empirical and theoretical relations have been formulated to describe phenomena of electric discharges in gases, which contain the "work functions" of metals for positive ions and for electrons.[1] The work function ϕ_- for electrons is defined as the work involved when an electron enters or leaves a metal. Similarly the work function ϕ_+ is the energy received by a metal when a positive ion transfers its charge to the metal.

[1] Güntherschulze, Zeits. f. Physik. **24,** 52 (1924); **31,** 509 (1925); **33,** 810 (1925); **37,** 868 (1926); Penning, Physica, **5,** 217 (1925); de Groot, Physica, **5,** 121, 234 (1925); Compton; Phys. Rev. **21,** 266 (1923); Schottky and von Issendorff, Zeits. f. Physik. **26,** 85 (1924), Seeliger, Phys. Zeits. **27,** 22 (1926).

Values of ϕ_- have been determined (1) by measuring the variation of thermionic emission of electrons with temperature and substituting in Richardson's equation[2]

$$j = AT^{1/2}\epsilon^{-e\phi_-/\kappa T};$$

(2) by measuring calorimetrically the heat of evaporation[3] of electrons; or (3) their heat of condensation[4]; (4) by use of Einstein's photoelectric equation[5]; (5) by use of Richardson's equation for the contact difference of potential between metals.[6]

With the single exception of von Issendorff's approximate values of ϕ_- for iron and nickel, in whose determination by method (3) important factors were neglected, all previously published values of ϕ_- have been obtained under conditions which render them of doubtful value in the theory of the gas discharge for one or more of the following reasons: (1) the gas pressure was made as low as possible for the express purpose of eliminating the effect of gas layers on the surface of the metal, as well as other complicating effects; (2) the metal had to be at a high temperature; (3) there was contamination of the cool metal by evaporation from the hot filament as in Cooke and Richardson's[4] determinations; (4) it was impossible to cleanse the surface *in situ*.

There have been no previous measurements of ϕ_+. When this quantity has been used in theoretical equations[7] its value has been calculated from a theoretical relation due to Schottky,[8] which is shown later in the paper to be based on an incomplete analysis of the phenomena involved in neutralization of positive ions at a metal surface.

The present work was undertaken to develop a method for measuring ϕ_- and ϕ_+ with as good precision as possible, for actual electrode surfaces in ionized gases, and to investigate the influence of various gases, electrode materials and surface treatments on these quantities. A preliminary report of some aspects of this work has already been published.[9]

Briefly, the general theory upon which the experimentation was based is as follows. If a Langmuir[10] collector is placed near the anode in a gaseous

[2] Richardson, Camb. Phil. Soc. Trans. **11,** 286 (1901); Phil. Mag. **201,** 497 (1903); Davisson and Germer, Phys. Rev. **20,** 300 (1922); Dushman, Rowe, Ewald and Kidner, Phys. Rev. **25,** 338 (1925).

[3] Wehnelt and Jentzsch, Verh. d. D. Phys. Ges. **10,** 610 (1908); Ann. d. Phys. **28,** 537 (1909): Cooke and Richardson, Phil. Mag. **25,** 624 (1913); **26,** 472 (1913); Lester, Phil. Mag. **31,** 197 (1916); Davisson and Germer, Ref. 2.

[4] Richardson and Cooke, Phil. Mag. **20,** 173 (1910); **21,** 404 (1911); Schottky and von Issendorff, Zeits. f. Physik. **26,** 85 (1924).

[5] Hughes, Photoelectricity p. 44, 1914; Hagenow, Phys. Rev. **13,** 415 (1919); Kazda, Phys. Rev. **26,** 643 (1925).

[6] Richardson, Phil. Mag. **23,** 264 (1912).

[7] Compton, Phys. Rev. **21,** 266 (1923); Schottky and von Issendorff, Zeits. f. Physik. **26,** 85 (1924).

[8] Schottky, Ann. d. Physik. **62,** 143 (1920).

[9] Compton and Van Voorhis, Proc. Nat. Acad. Sc. **13,** 336 (1927).

[10] Langmuir, Gen. Elec. Rev. **26,** 731 (1923); Science, **58,** 290 (1923); Jour. Frank. Inst. **196,** 751 (1923); Langmuir and Mott-Smith, Gen. Elec. Rev. **27,** 449, 538, 616, 762, 810 (1924).

discharge it will be surrounded by both positive ions and electrons. Now if its potential is maintained at a constant, slightly negative value V_o with respect to the space potential, positive ions will reach it at a constant rate due to their velocity of agitation in the gas, and the small attracting field V_o. Also electrons will reach it at a constant rate against the retarding field V_o because of the Maxwellian distribution of their velocities. Consequently in unit time the collector will receive an amount of heat H_o which is made up of: (1) the heat transfer by radiation H_r; (2) the heat transfer by conduction H_c; (3) the heat contribution of the positive ions due to their average energy of agitation, E_+ in the gas, their acceleration by the field, and their heat of neutralization at the metal surface; and (4) the heat contribution of the electrons due to their energy of agitation E_-, and their heat of condensation into the metal. Thus

$$H_0 = H_r + H_c + j^+(E_+ + V_0 + \phi_+) + j_0^-(E_- + \phi_-). \tag{1}$$

If the potential of the collector is then suddenly changed to a less negative value V_f there will be, immediately after the change, no appreciable variation of H_r and H_c, only a negligibly small change in j^+, but a large change in j^-. Hence

$$H_f = H_r + H_c + j^+(E_+ + V_f + \phi_+) + j_f^-(E_- + \phi_-). \tag{2}$$

Then subtracting Eq. (1) from Eq. (2)

$$H_f - H_0 = j^+(V_f - V_0) + (j_f^- - j_0^-)(E_- + \phi_-). \tag{3}$$

The difference H_f—H_o may be calculated from the heat capacity of the collector and its initial rate of temperature rise when the potential is changed from V_o to V_f. Then ϕ_- may be readily calculated since all of the remaining quantities on the right side of Eq. (3) are measured directly or are easily found by Langmuir's collector methods. In particular

$$E_- = \frac{0.869(V_f - V_0)}{\log_{10} j_f^-/j_0^-}. \tag{4}$$

In order to find ϕ_+, much larger potential differences and more negative potentials must be used in order to obtain larger variation of j^+ and to minimize the effect of j^-. Consequently other factors enter in, the full discussion of which will be taken up later.

The general idea of the investigation was therefore to measure the heating effect due to the condensation of known numbers of electrons or ions, measure and make allowance for their initial translational energies in the gas, and thence calculate the respective heats of condensation.

Apparatus

The discharge tube used in making the observations was constructed as shown in Fig. 1. It was essentially a low voltage arc tube to which was added a small spherical auxiliary electrode C, provided with a thermocouple

and located in the axis of the tube and distant about 1 cm from the nearest part *S* of the anode, on the side away from the filament *F*. The anode *A* was made of nickel and consisted of a cylindrical part fitting fairly closely to the walls, a small disk *S*, 1 cm in diameter, supported by two cross wires at the end of the cylinder, and a circular wing *W* placed at such an angle as to shield *C* from the reflected radiation of the 15 mil tungsten wire filament. The disk *S* served to shield *C* from the direct radiation from the filament and to minimize contamination of *C* by evaporated filament material.

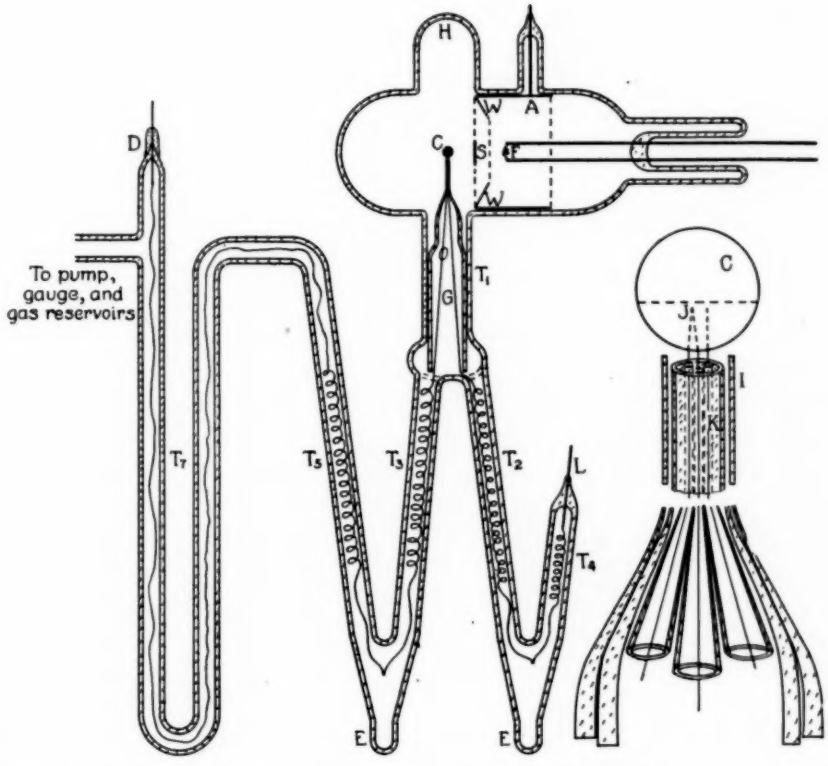

Fig. 1. Arrangement of apparatus and magnified sketch of collector mounting.

The sphere *C* was 3.4 mm in diameter, was made of molybdenum and was formed by drawing an arc between two vertical molybdenum wires in an atmosphere of hydrogen and allowing the arc to run until a bead of the desired size was formed on the upper wire. After this the bead was separated from the wire by grinding in such a way as to give an approximate sphere. Next, to prepare the sphere for mounting, a thin groove was cut nearly half way through it, by means of a thin saw blade and a sludge of fine carborundum in water, while being held firmly by means of two small hemispherical pits directly opposite each other in the leaves of a small steel hinge which was gripped in a vise. Then to free the sphere from hydrogen or any other gases which it might later give out from its interior, it was caged with molybdenum

wire on to a disc of molybdenum and the disk heated nearly to the melting point in a vacuum treating bottle, by means of high frequency induction currents. This heated the sphere to almost white heat, at which temperature it was maintained until no further evolution of gas could be detected. After a slight polishing to give a bright clean metal surface the weight of the sphere was accurately determined.

The method of mounting the sphere C is shown in the magnified side sketch in Fig. 1. The sphere was supported by three fine wires about 0.12 mm in diameter, two of which were copper and the third constantan, constituting the leads of the thermojunction J and a current lead. To keep these wires insulated from each other outside of C they were passed through the fine three-channeled glass tube K made by drawing down a larger tube in which had been placed three small thin-walled tubes. Another small thin-walled tube I surrounding K without touching it for at least 2 cm back from the end, and extending up almost to C, served to prevent any chance of electrical contact between any of the leads and whatever metal deposits might later be formed when C was bombarded to free it of gas layers. The lead wires and supporting glass tubes were kept as small as possible in order to minimize the conduction of heat away from the sphere. Good electrical and mechanical contact between C and the lead wires was obtained by placing their ends in the groove and squeezing it shut against them, using again the pitted iron hinge mentioned above, to prevent any considerable distortion of the sphere.

When the sphere had been mounted on its support the whole assembly was placed in a glass tube connected to an evacuating system and the thermocouple leads brought out through a "picein" wax joint. After annealing the thermocouple in vacuum at 500°C for about 60 hours it was calibrated at the steam, tin and sulphur points with the cold junction in an ice bath.

Next, the sphere was put into position in the discharge tube which had previously been connected up to the evacuating system by the connecting tubing shown in Fig. 1. The tube G supporting C fit snugly into the bottom tube T_1 of the discharge tube, and had been adjusted in length so as to bring C at the desired position with respect to S. Holes in the shoulder of G provided for the free passage of gases past it. When G was lowered into place through an opening in H, the previously coiled ends of the leads were guided down into the tubes T_2, T_3 and another similar one behind T_3. Then the ends of these lead wires, and of the ones which had previously been placed as shown in tubes T_4, T_5 and T_6 (behind T_5), were pulled out through the open ends E and melted together with a small reducing flame after which the junctions were drawn back into the tubes by the springs, thus allowing the glass tubes to be closed up. The current lead was brought out through a tungsten seal at L and the thermocouple leads out through small capillaries at D and at the end of the similar tube behind it, De Khotinsky wax being used to make these seals gas tight. This general arrangement was used so as to make it possible to change spheres without much difficulty; to eliminate the thermoelectric effects which might result if segments of tungsten were used to bring the thermocouple leads out through the glass; and to make it

possible to keep wax vapors out of the discharge tube, which was done by keeping liquid air around the U tubes T_7. This last precaution was proved to be quite necessary by the very erratic results obtained with an earlier tube having the leads coming out through wax seals in the bulb itself. Mercury vapor was prevented from ever reaching the U tubes by a stopcock and another liquid air trap which was always immersed in liquid air when the stopcock was open.

The discharge tube was surrounded by a tight box of quarter-inch asbestos board in which were placed heating coils so that the tube could be baked to a temperature of about 450°C, this box serving also to prevent temperature fluctuations which might result from air currents in the room during measurements. Care was always taken to keep the room temperature as constant as possible when observations were being made.

The electrical arrangements used are shown in Fig. 2.

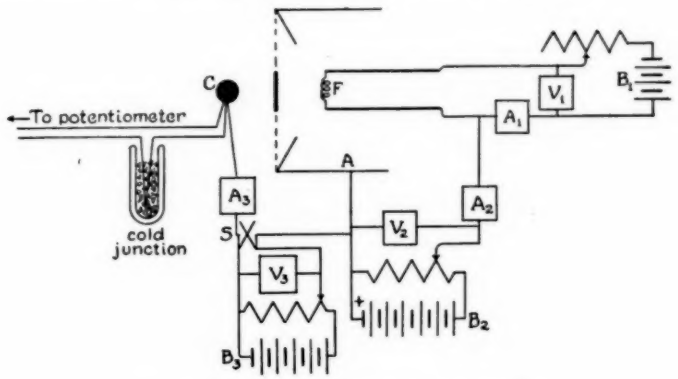

Fig. 2. Arrangement of electrical circuits.

The gases used in the discharge tube while carrying on this investigation were argon, hydrogen and nitrogen. The argon was purified by prolonged arcing between calcium electrodes in a bulb connected to the pumping system. The hydrogen was prepared by the electrolysis of a saturated solution of barium hydroxide and dried with phosphorus pentoxide. Waran's[11] method using ammonia and bromine was used to prepare the nitrogen. When a gas was admitted to the discharge tube it had to pass through both liquid air traps.

Methods of Observation and Calculation

1. *In the determination of* ϕ_-. The quantity $(H_f - H_o)$ of Eq. (3) was obtained from the product of the heat capacity Q of the collecting sphere C and the rate of temperature change dT/dt of C immediately after the change of potential from V_o to V_f. Since the temperature, starting at T_o when $t=0$, approached a final limiting value exponentially,

$$T - T_0 = (T_f - T_0)(1 - \epsilon^{-at}) \tag{5}$$

[11] Waran, Phil. Mag. **42**, 246 (1921).

where T was the temperature at time t, e the Naperian base, and a a constant dependent upon the existing experimental conditions. Then it follows from (5) that

$$\left(\frac{dT}{dt}\right)_{t=0} = a(T_f - T_0), \quad \text{where} \quad a = \frac{2.303}{t}\log_{10}\frac{T_f - T_0}{T_f - T}. \tag{6}$$

Consequently to obtain the data necessary to calculate a value of ϕ_- the procedure was as follows. The arc was first allowed to run for an hour or more to insure equilibrium conditions, particularly in regard to temperature. Then, using the sphere C as a Langmuir collector,[10] a set of current measurements was made over a voltage range from negative 30 volts with respect to the anode, to a potential well above that of the space. From this set of measurements could be obtained, by Langmuir's methods, the positive ion current j^+, the space potential V_s and the average energy E_- with which electrons reach the sphere when it is at a negative potential with respect to the space. Then, with the potential V_o of the collector somewhat negative to the space, the system was allowed to stand until the collector reached temperature equilibrium, when the conditions would be those represented in Eq. (1). After recording the current j_o to C, and electromotive force mV_o of the thermocouple, two stop watches were started simultaneously with a change of the sphere potential to some different negative value V_f. Then by slowly turning the drum of the potentiometer, the galvanometer deflection was kept as near zero as possible. At some instant when the deflection was exactly zero, one watch was stopped and the time t_1, and corresponding mV_1, were recorded, after which mV_2 was measured in the same way for time t_2 obtained by means of the second watch. As soon as the temperature became practically constant, which was generally about 5 minutes after t_o, record was made of mV_f. This gave the data for calculating two values of the quantity a, and the mean of the two $\bar{a}$ was used in applying Eq. (6).

In Table I are tabulated typical sets of observations and the resulting quantities obtained from the various steps in the calculating of ϕ_-. In column 2, j_o and j_f are the total collector currents in milliamperes, while j^+ is the positive ion current and is the amount to be added to j_o and j_f to give j_o^- and j_f^-. The value of j^+ was determined in the usual way,[10] *i.e.*, by plotting positive ion currents against applied voltages which were enough negative to the space to prevent any appreciable number of electrons from reaching the collector. This gave a practically straight line with small slope, whose extension gave j^+ at V_o.

To obtain the temperature differences given in column 5 the corresponding millivolt differences obtained from column 4 were divided by the millivolt differences per degree of the electromotive force of the thermocouple at the corresponding temperatures. The temperatures and corresponding millivolt differences per degree were readily determined from two curves obtained by plotting against temperature on a large piece of graph paper, the values

of mV and $d(mV)/dT$ calculated at 20° intervals from the calibration equation of the thermocouple, $mV_T = .0400766T + .00004344T^2 - .00000002244T^3$.

For the sake of conserving space, two independent quantities are tabulated in column 8, Q being the heat capacity of the collector in milli-joules per degree, and C^+ the quantity arising out of the term $j^+(V_f - V_o)$ in Eq. (3), which quantity had to be added to the product of the quantity in column 7, times Q, to give $(E_- + \phi_-)$. The values of E_- in column 10 were calculated by means of Eq. (4).

TABLE I

Typical sets of data and quantities obtained in the determination of ϕ_- for molybdenum in pure nitrogen.

The first two sets of observations were taken in close succession about two hours after pure nitrogen had been placed in the arc tube; the third set was one of several similar ones taken after the nitrogen had remained in the tube over night, and the last three were taken in succession after bombarding the collector for 1 minute with a 0.2 milliampere positive ion current under an applied potential of about 550 volts.

1	2	3	4	5	6	7	8	9	10	11
$V_f - V_0$	j_0 j_f j^+	t_0 t_1 t_2 t_f	mV_0 mV_1 mV_2 mV_f	$T_f - T_0$ $T_f - T_1$ $T_f - T_2$	a_1 a_2 $\bar{a}$	$\frac{(T_f - T_0)\bar{a}}{j_f^- - j_0^-}$	Q C^+	$E_- + \phi_-$	E_-	ϕ_-
volts	ma.	sec.	millivolts	°C				volts	volts	volts
	0.390	0	9.135	5.510						
0.632	1.615	24.5	9.255	3.303	.02090	.0937	60.90	5.73	0.93	4.80
	0.034	53.4	9.336	1.814	.02080					
		∞	9.435		.02085		0.02			
	0.395	0	9.095	5.335						
0.613	1.585	23.7	9.209	3.234	.02112	.0944	60.88	5.77	0.92	4.85
	0.034	53.2	9.290	1.744	.02100					
		∞	9.385		.02106		0.02			
	0.395	0	9.220	5.595						
0.652	1.600	20.6	9.325	3.662	.02050	.0951	60.95	5.81	0.98	4.83
	0.037	56.0	9.428	1.775	.02050					
		∞	9.525		.02050		0.02			
	0.475	0	9.130	8.524						
0.679	2.290	26.2	9.325	4.945	.02080	.0970	60.95	5.92	0.90	5.02
	0.035	55.0	9.444	2.763	.02050					
		∞	9.595		.02065		0.01			
	0.505	0	9.085	7.895						
0.631	2.205	35.0	9.305	3.849	.02052	.0958	60.92	5.85	0.89	4.96
	0.035	66.0	9.405	2.013	.02070					
		∞	9.515		.02061		0.01			
	0.500	0	9.032	8.275						
0.630	2.225	24.6	9.208	5.028	.02024	.0961	60.90	5.86	0.87	4.99
	0.035	56.9	9.336	2.676	.01984					
		∞	9.482		.02004		0.01			

The observations for determining ϕ_- in argon were made with the gas pressure about 0.5 mm and a 16 volt 160 milliampere arc running, since under these conditions conveniently large electron currents to the collector could be obtained at potentials well below the space potential, and also the probability that a positive ion would make a collision while passing through

the space charge sheath was small, thus practically eliminating any uncertainty which such collisions might introduce in the extrapolated value of j^+. In pure nitrogen the same pressure and a 20 volt 120 milliampere arc were used. It was found that a sufficiently strong low voltage arc could not be easily maintained in pure hydrogen, consequently mixtures containing from 50 to 90 percent of argon were used, and the pressure had to be reduced to about 0.3 mm in order to obtain suitable arc currents (from 40 to 120 milliamperes) with 20 volts across the tube.

When making a series of observations with a given gas, the collector was frequently bombarded with high velocity positive ions for about a minute at a time, in order to change the surface condition, if this could be done, *i.e.*, if the existing surface condition were not the one truly characteristic of the gas. If successive bombardments produced rather variable results contamination of the gas was suspected, whereupon the arc tube was evacuated and refilled with a fresh supply of the pure gas. This process was repeated until bombardment produced no change in results, or only consistent, repeatable changes which will be discussed later. After hydrogen had been used in the tube it was especially difficult to remove the effects of this gas so completely that the characteristic value of ϕ_- in argon or nitrogen could again be obtained, but this could be done by repeated bombardments and flushings with argon.

2. *In the determination of* ϕ_+. In this part of the investigation the arc was maintained in pure argon, since the positive ion currents in nitrogen arcs were found to be much smaller than in argon arcs. To obtain positive ion currents considerably larger than those found under the conditions existing when ϕ_- was investigated, the arc current was increased to about 400 milliamperes by increasing the filament temperature. However, when this was done with the pressure kept at about 0.5 mm the semi-logarithmic plot of the electron current (to C) against the applied voltage indicated the presence of a large number of the high speed "secondary" electrons discussed by Langmuir.[12] To minimize the disturbing effect which these high speed electrons might have upon the experimental results, their concentration was greatly reduced by increasing the pressure to 1.0 mm or more.

At first sight the simplest method of determining ϕ_+ would seem also to be by use of Eqs. (1) and (2), making V_o and V_f sufficiently negative to prevent practically all electrons from reaching the collector and making $(V_f - V_o)$ sufficiently large to give accurately measurable values of $(j_f^+ - j_o^+)$ and of $(dT/dt)_{t=o}$. Under such conditions we have

$$H_f - H_0 = (j_f^+ - j_0^+)(E_+ + \phi_+) + j_f^+ V_f - j_0^+ V_0. \tag{7}$$

This equation would be valid if the positive ions lost no energy at collisions with neutral atoms while passing through the space charge sheath which surrounded the collector. Experimental test of the equation showed that the loss of energy resulting from collisions was an important factor,

[12] Langmuir, Phys. Rev. **26**, 585 (1925).

for without taking it into account in the calculations, two sets of observations gave for $(E_+ + \phi_+)$ the absurd values of -75 and -55 volts respectively. Though this method could not be used to find ϕ_+ directly, it could be used to obtain the correction which must be made for energy losses at collisions, as will be fully described later.

The procedure actually followed in obtaining data for the calculation of ϕ_+ was based upon the following considerations. When the equilibrium temperature of the collector is followed as its potential is made more and more negative with respect to the space, a potential is found for which the temperature is a minimum. For more negative potentials the increase in heating effect of the positive ions because of both their increasing number and their greater acceleration, overbalances the decrease in heating effect of the electrons due to their decreasing numbers, whereas for less negative potentials the increase in heating effect of the electrons is greater than the decrease in the effect of the positive ions. Consequently there will be, in general, two potentials which will produce the same heating effect at the collector. Calling these potentials with respect to the space, V_o and V_f as before, and representing by $F_o(V_o)$ and $F_f(V_f)$ the respective energies which the positive ions have retained after suffering collisions in passing through the sheath, *i.e.*, the average energies with which they strike the collector under the influence of the respective potentials, the equation which expresses this equality of heating is

$$j_f^+\{F_f(V_f)+E_+ +\phi_+\}+j_f^-(E_- +\phi_-)=j_0^+\{F_0(V_0)+E_+ +\phi_+\}+j_0^-(E_- +\phi_-) \quad (8)$$

Thus in the method based upon this equation the determination of the rate of temperature change was not involved, and consequently this possible source of considerable error was eliminated.

As a convenient value of V_o, the potential at which equal numbers of positive ions and electrons reached the collector was used since the collector would take up its equilibrium condition for this potential when insulated, as with the switch S open. Consequently the switch needed to be closed only a very short time when determining the potential V_o giving zero current through A_3, or when determining the potential V_f giving a fairly large positive current j_f through A_3 but producing the same temperature in the collector as open circuit. All but the final small adjustments of the potential divider were made with the switch open. In this way the observations could be taken rapidly so that the gradual fluctuations of the room temperature would have no appreciable effect upon the results.

Immediately after a series of the observations just described had been made, a set of current measurements over a wide range of potentials was taken just as was done preliminary to taking data for calculating ϕ_-. From these current measurements were obtained the electron currents at various potentials, and by means of their semi-log plot the average energies of the two groups of electrons as well as the currents at V_o and V_f resulting from each group, were found. To distinguish the two groups of electrons from each other, all quantities involving the faster group will be primed, thus

$j_o^+ = j_o'^- + j_o^-$. The extrapolated semi-log plot of the slower electrons showed that their number was negligibly small at V_f, consequently $j_f^+ = j_f + j_o'^-$. Taking account of the two groups of electrons Eq. (8) takes the form

$$(j_f^+ - j_0^+)(E_+ + \phi_+) = j_0^+ \cdot F_0(V_0) - j_f^+ \cdot F_f(V_f) + j_0^-(E_- + \phi_-) + (j_0'^- - j_f'^-)(E_-' - \phi_-) \tag{9}$$

In order to determine $F_o(V_o)$ and $F_f(V_f)$, the number of collisions made within the sheath and the fraction of energy retained after each collision had to be found. That the sheath thickness when the positive ions made collisions within the sheath, could not be calculated by means of the Langmuir[10, 13] equation for spherical electrodes (which assumes no collisions) was shown by the fact that the results obtained by this method led to widely varying values for the positive ion concentration in the discharge, when based on measurements at different electrode potentials. The sheath thickness was actually found by extending the approximately straight positive ion current-voltage line to the space potential and thus obtaining from the known surface of the collector and the extrapolated value of the positive ion current, the rate at which positive ions crossed unit area in the space. From this rate, the sheath area and thence the thickness of the sheath for any given value of j^+ could be calculated. Since the positive ions in all the cases where these calculations were made had velocities rather large in comparison with those of the neutral gas molecules, their mean free path was taken to be $\sqrt{2}$ times the kinetic theory value for a molecule at the given pressure and temperature.

If y be the fraction of its energy retained by a positive ion after a collision and if, in order to simplify the calculations, it be assumed that the potential drop across the space charge sheath is uniform,[14] it can be shown that as the result of an integral number n of collisions made by a positive ion falling through a potential drop V across the sheath

$$F(V) = \frac{V}{n}\left(y + y^2 + \cdots y^{n-1} + \frac{y^n + 1}{2}\right). \tag{10}$$

If the average number of collisions be a proper fraction f, then $F(V)$ must be obtained from the equation

[13] Langmuir and Blodgett, Phys. Rev. **24**, 49 (1924).

[14] If V_s represents the potential at the surface of the sheath and V_x that at a point within the sheath a distance x from the surface, instead of $V_x - V_s \propto x$ in accord with the above assumption, probably $V_x - V_s \propto x^b$ approximately, where the exponent b would have a value between 4/3 and 2. The lower limit is the one obtained from the space charge equation, for the case of no collisions or ionization, and the upper limit is obtained from Aston's measurements (Proc. Roy. Soc. London, **A84**, 526 (1911)) of the potential distribution in the abnormal cathode fall space, where the positive ions made numerous collisions and there was probably considerable ionization taking place within the sheath. Though the simplifying assumption is not in exact accord with the actual conditions, from considerations which will be discussed later it is believed that the use of this assumption does not introduce any large error into the results.

$$F(V)=V\left\{1-\frac{f(1-y)}{2}\right\}. \tag{11}$$

To obtain $F(V)$ for a given y and an average number of collisions m, which was a mixed number, the values of $F(V)$ for several integral numbers were calculated from Eq. (10) and from the plotted curve of these values, that for m collisions could be read off directly.

It was evident from the absurd values of $(E_+ + \phi_+)$ obtained from Eq. (7) that the first term on the right side of the equation was small in comparison with the other terms, consequently for a first approximate calculation of y, the equation

$$H_f - H_0 = j_f^+ \cdot F_f(V_f) - j_0^+ \cdot F_0(V_0) \tag{12}$$

could be used. In column 2 of Table II are tabulated the positive ion currents obtained at the potentials given in column 1. These observations were made

TABLE II

Calculation of y, the fraction of energy retained by a positive ion after a collision.

1 V_0 V_f	2 j_0^+ j_f^+	3 Number of Collisions	4 Observed $H_f - H_0$	5 Calculated values of $H_f - H_0$ For $y=1.0$	6 For $y=0.8$	7 For $y=0.75$	8 Percent difference in values of a	9 Weighted estimate of value of y
Volts	milliamps.			milliampere-volts				
17.1	0.402	.75						
32.1	0.4425	1.20	5.88	7.33	6.14	5.88	7%	
17.05	0.402	.77						
32.1	0.441	1.22	5.62	7.30	6.11	5.84	4%	
17.05	0.400	.76						
32.0	0.4395	1.21	5.58	7.24	6.06	5.79	1%	0.73
31.8	0.437	1.21						
46.8	0.473	1.60	5.65	8.21	6.44	6.02	3%	
31.8	0.4375	1.23						
46.8	0.474	1.63	5.80	8.23	6.43	5.99	1%	
31.8	0.4355	1.23						
46.7	0.470	1.58	5.75	8.09	6.40	6.00	3%	0.73
46.7	0.4695	1.61						
61.5	0.5025	1.94	6.39	8.99	6.67	6.18	4%	
46.3	0.4705	1.64						
61.5	0.5075	2.02	6.22	9.45	6.91	6.35	0%	
46.2	0.4675	1.61						
61.4	0.500	1.95	6.56	9.10	6.67	6.40	4%	0.75

in argon at a pressure of 1.0 mm and the temperature of the collector ranged from 233° to 243°. Assuming that the temperature in the sheath was the same as that of the collector, the average number of collisions given in column 3 was calculated from sheath thickness, as described. The values

of $(H_f - H_o)$ recorded in column 4 were calculated by exactly the same method as was used in the determination of ϕ_-. The theoretical values which $(H_f - H_o)$ should have when y is equal to 1.0, 0.8 and 0.75 respectively, were obtained by calculating the value of the right side of Eq. (12) by the method described in the discussion of Eq. (10) and are recorded in columns 5, 6, and 7. A comparison of these values with the observed ones in column 4, taking into account the probable relative accuracies of the values in column 4 as indicated by column 8, led to the estimated values of y for the different voltage intervals, which are recorded in column 9. By extrapolation of the curve of these estimated values of y plotted against the average potentials for which they were calculated, were obtained the proper values of y to be used in obtaining $F_o(V_o)$ and $F_f(V_f)$ in Eq. (9).

Having now described the methods of obtaining all the quantities on the right side of Eq. (9), we pass to an example of the actual calculation of $(E_+ + \phi_+)$ from data obtained by the method outlined in the discussion of Eq. (8). In the first three columns of Table III are tabulated the potentials

TABLE III

Calculation of $(E_+ + \phi_+)$ in argon.

1	2	3	4	5	6 7	8	9	
V_0	$j_0'^-$	$j_f'^-$	f_f	$-j_f^+ \cdot F_f(V_f)$	$j_0^-(E_- + \phi_-)$	Sum of 5 & 6	$j_f^+ - j_0^+$	$E_+ + \phi_+$
V_f	j_0^-			$+j_0^+ \cdot F_0(V_0)$	$(j_0'^- - j_f'^-)(E_-' + \phi_-)$			
	j_0^+	$j_f'^+$	f_i					
volts	ma.	ma.		ma.-volts	ma.-volts		ma.	volts
2.634	.0645	.3475	.11	−3.010	1.598			
9.00	.2696	.0036				.037	.0170	2.18
	.3341	.3511	.34	.868	.581			
2.644	.0642	.3465	.10	−3.002	1.595			
8.97	.2690	.0036				.038	.0169	2.25
	.3332	.3501	.33	.867	.578			
2.656	.0639	.3460	.10	−2.992	1.594			
8.95	.2689	.0036				.049	.0168	2.91
	.3328	.3496	.33	.872	.575			
2.661	.0637	.3455	.10	−2.988	1.594			
8.94	.2688	.0037				.051	.0167	3.05
	.3325	.3492	.33	.873	.572			
2.663	.0635	.3445	.09	−2.980	1.589			
8.94	.2680	.0037				.051	.0167	3.05
	.3315	.3482	.32	.872	.570			

with respect to the space, and the various current components which had been determined by the method described just previous to the statement of Eq. (9). Column 4 gives the calculated average number of collisions made by the positive ions in passing through the sheath. The algebraic sum of the quantities in columns 5 and 6, which is recorded in column 7 gives the calculated value of the right side of Eq. (9) in milliampere-volts. The value of $(E_+ + \phi_+)$ recorded in column 9 was obtained by dividing this sum by the quantity $(j_f^+ - j_o^+)$ given in column 8. Since $(E_+ + \phi_+)$ was comparatively

small, a second order calculation of y in which the term involving $(E_+ + \phi_+)$ was taken into account, produced only a small change in the value of y, and this in turn led to a negligibly small change in $(E_+ + \phi_+)$.

Determination of $(E_+ + \phi_+)$ in argon was made at the two gas pressures, 1.8 mm and 1.0 mm. The actual procedure followed in making the observations for calculating $(E_+ + \phi_+)$ at a given pressure, consisted of six steps. (A) Four or more sets of observations were made of the potential to give zero current, and of the more negative potential which produced the same heating, and also of the net current at the latter potential. (B) The currents over a large range of voltages were measured, from which measurements were to be obtained: (a) the actual positive ion and electron currents at the potentials observed in step (A); (b) the velocities of agitation in the two groups of electrons, and the fraction of the electron currents due to each group; and (c) the positive ion drift across unit area in the space, which was to be used in calculating the number of collisions within the sheath. (C) The sets of data such as used in Table II for the calculation of y were next taken. (D) Then several sets of observations for obtaining the actual value of ϕ_- under the *existing* conditions were made, since a very slight amount of impurity might affect this value considerably. As soon as possible after (D) steps (A) and (B) were repeated. Though no adjustment of the arc conditions was made during this entire procedure there was a very slow decrease in the arc current, which was probably due to a gradual decrease in the voltage of the filament battery. Consequently a record was kept of the time at which each observation was made, and the arc current was recorded at frequent intervals, so that correction could be made for the change of arc current taking place during the intervals between the taking of the different types of observations. The series of observations above described furnished the data for the calculation of two separate series of values for $(E_+ + \phi_+)$.

Tabulation and Discussion of Results

Consideration of the available data on the specific heat of molybdenum. The apparatus had been set up and a series of observations taken before it was discovered that the published measurements of the specific heat of molybdenum are meager and not very consistent. It was deemed advisable, however, to go on with the measurements with the molybdenum collector since the results could easily be corrected, if necessary, when more satisfactory specific heat data became available. In Fig. 3 are shown all of the specific heat values for molybdenum which could be found in the literature, except values for very low temperatures and the values by Wüst for temperatures above 300°C.

The equations of the lines I, II and III are:

$$C_T = 0.0640 + 0.000032T \quad \text{(I)}$$

$$C_T = 0.0606 + 0.000028T \quad \text{(II)}$$

$$C_T = 0.0578 + 0.0000257T \quad \text{(III)}$$

where T is the Centigrade temperature. Eq. (I) was obtained from the straight line which seemed to the author to give the best fit with the experimental data when all values were given equal weight,[15] and was the one used in making all of the original calculations among which were the ones given so far in this paper. When it was learned that Eq. (III),[16] which is based largely on theoretical considerations, was used in the General Electric Company's Research Laboratory, the previously obtained results were recalculated using this equation. Since this recalculation gave values for $(E_+ + \phi_+)$ which seemed to be unreasonable, as will be shown when discussing

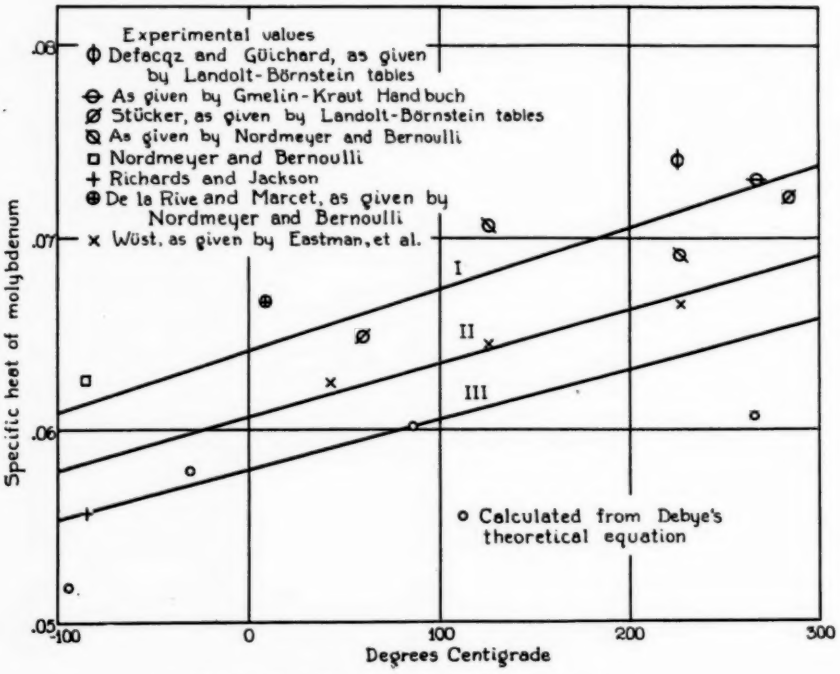

Fig. 3. Specific heat values for molybdenum.

the results, it seemed probable that Eq. (III) gives too low values of the specific heat. It was deemed advisable to calculate the results also on the basis of an intermediate equation so that when satisfactory specific heat data become available the correct results may be easily obtained by interpolation. Eq. (II) is the intermediate equation used and is one which gives very close agreement between the value of ϕ_- of molybdenum, as determined in argon in this investigation, and the value given by Dushman[17] when the

[15] The measurements of Wüst (Ver. Deutsch. Ing. Forschungarb. No. **204** (1918). cf Eastman, Williams and Young, Jour. Am. Chem. Soc. **46,** 1184 (1924)), were unknown to the author when Eq. (I) was obtained.

[16] We are indebted to Dr. H. A. Jones of the General Electric Company's Research Laboratory for giving us the values obtained from the theoretical calculations, and also the specific heat equation for molybdenum which is used in that Laboratory.

[17] Dushman, Phys. Rev. **21,** 623 (1923).

latter has been adjusted[18] for the temperature (200°C) at which the present measurements were made.

Results for ϕ_-. In the last three columns of Table IV are given the mean values of ϕ_- as calculated when using the specific heat Eqs. (I), (II) and (III)

TABLE IV

Values of ϕ_- for molybdenum.

Gas	Average Temperature	Number of values averaged	ϕ_- in volts I	II	III
Argon	200°C	20	4.76	4.39	4.12
Argon-hydrogen mixture	200°	24	4.35	4.04	3.79
	208°	25	4.04	3.70	3.47
Nitrogen	196°	20	4.77	4.43	4.18
	197°	13	5.01	4.66	4.39

respectively. The average temperatures are given also, since they will be useful if other specific heat data are used to correct these results. Of the two values of ϕ_- obtained with hydrogen present, perhaps one is due to an atomic layer and the other to a molecular layer on the collector. The lower of these two values was usually obtained when there was a large quantity of hydrogen present, and just after the collector had been bombarded with positive ions accelerated by a potential of 500 volts. The higher value was the one which persisted for a long time when the tube was being freed of hydrogen preparatory to taking further readings in argon or nitrogen. It was not found possible to control conditions so that one value could be obtained repeatedly with the complete exclusion of the other. The values would change suddenly from either one to the other when there had been no noticeable change in the experimental conditions. This effect was at first very disconcerting as the results seemed so variable that they did not seem to be reliable, and it was only after a considerable number of values had been obtained none of which came between 4.12 and 4.26 volts that the true state of affairs became apparent.

Two values of ϕ_- were obtained also in nitrogen, the lower one of which is seen to be almost identically the same as ϕ_- in argon. The higher value was obtained only after the collector had been bombarded in the regular way by positive ions, the results given in Table I being typical ones for this gas. From the fact that Langmuir[19] found the electron emission from a tungsten filament to be unaffected by the presence of a small amount of

[18] The temperature adjustments of ϕ_- mentioned here and later, have been made by means of the following equation given by Davisson and Germer[2]

$$\phi_T \text{ (calorimetric)} = \phi_0 + 2kT/e$$

where k is the Boltzmann gas constant, e the charge on an electron and T the absolute temperature.

[19] Langmuir, Phys. Rev. **2**, 450 (1913).

argon, it is not unreasonable to assume that argon does not form such a layer on the surface of the collector as would affect the work function of the metal. If this assumption be true, it would seem to be possible also for nitrogen positive ions and gas molecules to strike a molybdenum surface without forming a layer which would affect ϕ_-, although when the positive ions strike with high velocities such a layer is formed. Consequently nitrogen might affect the value of the work function at the cathode, and yet have no effect upon its value at the anode of a discharge tube.

Except for the uncertainty due to the specific heat values, the results for ϕ_- are believed to be accurate to within about 1 percent. Most of the determinations of any one value were within 1 percent of the mean and only a very few varied from it by as much as 2 percent, even though for every one of the five values the results averaged were obtained at two or more different times between which measurements had been made on one or both of the other gases. Consequently the effects which hydrogen and nitrogen have on the electron work function of molybdenum have been found, even though the actual magnitudes of these effects may still be a little uncertain.

It may not be out of place to note here some values of ϕ_- for molybdenum obtained by other observers using other methods. As adjusted[18] for 200° Lester[3] found 4.35; Stoeckle,[20] 4.70; Dushman,[17] 4.39; and calculations from two sets of slope observations reported by Dushman and collaborators[2] give 4.63 and 4.52 respectively. These values would indicate that the true specific heat line should lie somewhere between I and II in Fig. 3.

Results of ϕ_+ in argon. The three sets of results for $(E_+ + \phi_+)$ as calculated on the basis of the three specific heat equations, are given in Table V. The

TABLE V

Values of $(E_+ + \phi_+)$ for molybdenum in argon.

Average Temperature	Number of determinations in the series	$(E_+ + \phi_+)$ in volts I	II	III	Weight
223°C	4	−1.8	−9.5	−12.0	1
219°	6	+1.9	−6.4	−10.7	1
231°	5	−1.1	−5.5	− 9.8	1
228°	5	+2.7	−2.0	− 5.9	3
Weighted mean		+1.2	−4.6	− 8.0	
Probable values of ϕ_+ obtained by taking $E_+ = 0.4$ volt.		.8	−5.0	− 8.4	

last set of values has been given triple weight because of more satisfactory experimental conditions and technique. As may be seen in Table III, the quantity from which a value of $(E_+ + \phi_+)$ is ultimately determined is the small difference between two rather large calculated quantities, consequently it is to be expected that the results might vary considerably. However, since

[20] Stoeckle, Phys. Rev. **8**, 534 (1916).

it is believed that no large systematic error has entered into the calculations, the errors should be compensating. Though the assumption[14] in regard to the potential distribution in the sheath is not in actual accord with theory and experiment, the error which might enter from this source is believed to be very small owing to the extremely small number of collisions made and the use of a value for the fraction of energy retained after a collision, which was obtained by a short extrapolation to the potential actually used. An error of 1 volt in the determination of the space potential would make a change of only about 0.3 of a volt in the result for $(E_+ + \phi_+)$. Consequently except for the uncertainty arising from the specific heat values used, it is believed that the error in the mean value can not be more than 2 volts, and probably is considerably less than that.

The value of E_+ was not measured, but from Langmuir's[10] observation that E_+ usually has a value between $E_-/3$ and $E_-/2$, 0.4 volt seems to be a reasonable value to use here. Thus the value of ϕ_+ obtained on the basis of the specific heat Eq. (III) has so large a negative value as to be unreasonable. Even the value obtained with Eq. (1) is much lower than would be expected from the theoretical equation $\phi_+ = V_i - \phi_- + L$ proposed by Schottky[8] and later by Compton.[7] According to this equation, at a molybdenum target in argon, $\phi_+ = 15.3 - 4.8 = 10.5$ volts, L in this case being zero since there is no (net) condensation of the gas molecules.

However, as a possible explanation of the fact that ϕ_+ seems to be much lower than would be expected from Schottky's equation, I wish to propose the following view as to the mechanism accompanying the neutralization of an argon positive ion at a metal surface. As the positive ion becomes neutralized at the surface of the metal, its combination with an electron probably occurs before the ion has made actual thermal contact with the metal. Thus the energy of neutralization may be given up by radiation in all directions and the metal would be heated only by the absorbed portion of the radiation which strikes it. On this view

$$\phi_+ = aV_i/2 - \phi_- \tag{13}$$

in which a is the fraction of the incident radiation absorbed by the metal. Thus, by using the value of 0.8 for ϕ_+ we obtain 0.73 for the value of a, which is a very reasonable value when considered in connection with Hulburt's[21] measurements of the reflecting power of molybdenum for ultraviolet light.

If this view of the neutralization mechanism for a *gas* positive ion at a metal surface be correct, it would seem probable that somewhat the same process may take place when *metallic* positive ions condense into the cathode, since all, or at least a part, of the energy of neutralization may be radiated before the atom actually becomes an integral part of the solid or liquid metal. An inference from this would be that the values of ϕ_+ which Günther-schulze[1] has calculated for various metals, are too large.

[21] Hulburt, Astrophys. J. **42**, 205 (1915).

Confirmatory evidence of the pressure of a group of high speed (secondary) electrons in a gaseous discharge at low pressure. The correctness of Langmuir's[12] conclusion that two distinct Maxwellian velocity groups of electrons may be found in a low pressure, high current gas discharge was shown in the following way. With a 400 milliampere arc in argon at about 0.4 mm pressure, observations such as those used to calculate ϕ_- were taken over a rather wide range of voltages. These measurements were used, not to calculate ϕ_-, but to determine the average energy E_- of the electrons reaching the collector at the various voltages, using in these calculations the value of ϕ_- previously determined. In Fig. 4 are plotted the logarithms of the electron currents,

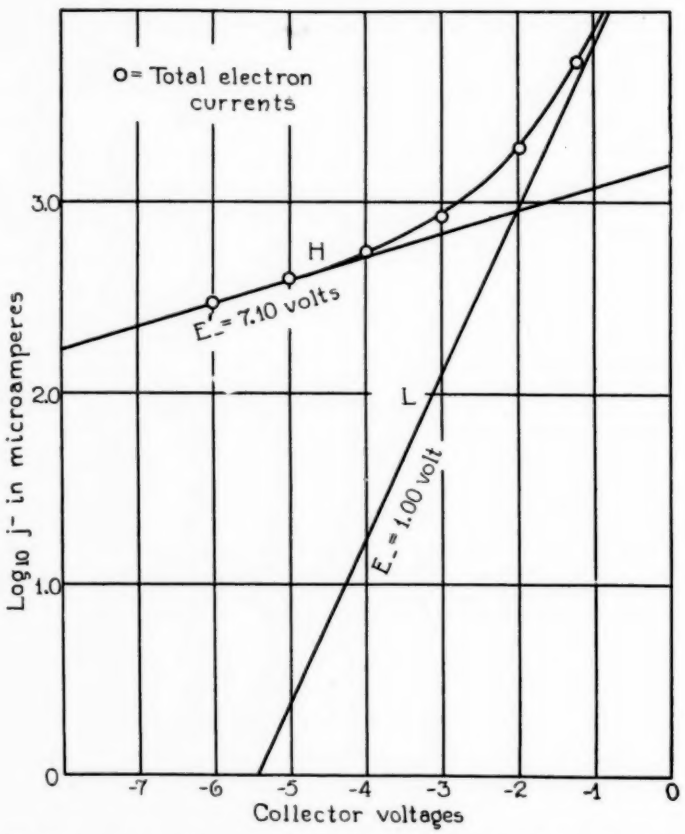

Fig. 4. Variation with collector voltage of the logarithm of the total electron current and of the *secondary* and *ultimate* electron current components.

against the voltages at which they were obtained, and also the lines H and L showing the average energy of the *secondary* and *ultimate* electrons respectively (which crossed a surface), as well as the contribution of each group to the current at the different voltages. In Table VI the values in the second and third columns were calculated by methods described for the calculations of ϕ_-, *i.e.*, the second column gives the values obtained by multiplying Q by quantities obtained in the same way as those in column 7 of Table I. The

values in the third column correspond to C^+ of column 8, Table I. The last three columns give respectively the values of E_- as obtained calorimetrically, as calculated from the equations of the lines H and L in Fig. 4, and as calculated by Eq. (4).

TABLE VI

Confirmatory evidence for the presence of two groups of electrons with widely different Maxwellian velocities.
All values are given in volts.

V_0 V_f	Net heating per electron	Decrease in positive ion energy per electron	$(E_-+\phi_-)$ Total heating per electron	Average energy of the electrons E_-		
				$(E_-+\phi_-)$ minus 4.76	Calculated from group plots in Fig. 4	Calculated by Eq. (4)
−6.00 −5.00	2.49	9.44	11.93	7.17	6.95	6.95
−5.00 −4.00	4.87	6.34	11.21	6.45	6.40	6.48
−4.00 −3.00	5.91	3.40	9.31	4.57	4.58	4.67
−3.00 −2.00	6.17	.90	7.07	2.31	2.25	2.37
−2.00 −1.23	6.12	.20	6.32	1.56	1.42	1.50

It has been suggested that the "high speed" electrons are not real, but only apparent, and that the real explanation of the change in slope in electron current curves like that in Fig. 4, is the occurrence of very high frequency oscillations in the potential of the collector. If such oscillations occur, it is true that they might give such a current-voltage curve, but that they could produce heating effects similar to those of high speed electrons does not seem possible since the mean energy of the incoming electrons is independent of the potential of the collector, provided this is negative as in the present work. The good agreement of the values of electron energies calculated calorimetrically, with those obtained on the assumption of a group of high speed electrons, is thus convincing evidence of the real existence of such high speed electrons. As was mentioned before, the collector was completely shielded from the direct radiation of the filament and consequently from *primary* electrons, so that it gave no evidence of their presence in the discharge.

Further applications of the method. It is planned to extend the measurements by this method to other gases and to other metals. This method should be particularly useful in determining ϕ_- of metals which cannot be investigated thermionically, thus giving a check upon the values obtained by photo-electric methods. Also it is believed that important information may be obtained by using this method in the study of effects due to thin layers of alkali and alkaline earth metals on the electrodes in a gas discharge. A slight modification of the tube will make it possible to measure the contact

difference of potential between two metals when under exactly the same conditions as to gas layers, and to measure the effect of such gas layers upon the contact differences of potential.

In conclusion I wish to express my thanks to Professor K. T. Compton who proposed this investigation and who has made many helpful suggestions while it has been in progress.

PALMER PHYSICAL LABORATORY,
PRINCETON, NEW JERSEY.
May 28, 1927.

ON THE EFFECT OF THE MEDIUM ON GAS ION MOBILITY

By Henry A. Erikson

Abstract

Effect on the mobility of air ions of adding varying amounts of CO_2, H_2, water vapor, C_2H_2, C_2H_4, Cl_2 and NH_3 to the medium.—In this paper results are given showing the effect on the mobility of adding foreign gases to the air through which the ions move. The conditions were such as to permit the use, at least initially, of identical air ions. It is shown that adding CO_2 and water vapor to the air diminishes the mobility but adding hydrogen increases the mobility. The results also indicate that the change in the mobility is due to the change in the medium and not to a change in the ions. It is however found that increasing the relative humidity gives a larger proportion of initial or 1.87 ions indicating that H_2O simplifies the final positive air ion. It is also shown that a trace of acetylene gives rise to an ion which has a mobility only slightly less than the initial air ion. It was also found that when acetylene remains in air a body is formed which when it becomes charged has a lower mobility.

Results are also given showing that adding ethylene and chlorine to the air has no effect on the mobility within the time of observation used whereas a trace of ammonia results in the formation of a single positive ion of the same mobility as that of the negative ion which is not affected.

THE speed with which an ion moves through dry air at normal pressure and temperature under the action of an electric field depends upon the charge carried by the ion and on the complexity of its structure as regards aggregation of molecules. All singly charged molecules have practically the same mobility as the mass plays only an insignificant part. The speed with which a given ion travels depends also upon the nature of the gaseous medium through which it moves. In this paper are given a number of results showing the effect upon the mobility of changing the nature of the medium by adding foreign gases in varying amounts. The method used

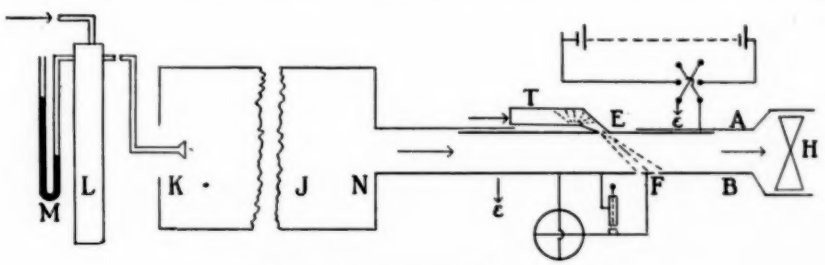

Fig. 1. Arrangement of apparatus.

consisted in passing ions of a definite character across a stream of the air to which the foreign gas had been added. The arrangement of the apparatus is shown in Fig. 1. The ions were produced in the tube T and at E they entered the air stream where they were forced across the stream by the

field between the plates A and B to the electrode F, the downstream distance of which could be altered. The current to F plotted against the downstream distance of F gives a curve the position of the maximum of which depends upon the mobility. The air stream between the plates A and B due to the fan H, was taken from a large mixing tank J into which it entered from the room through an opening at K. The speed of the stream was of the order of 500 cm/sec. The foreign gas was added to the air near K and in passing through the tank J was mixed with the air. The effect on the mobility, of adding the gas in varying amounts, was noted.

Experimental Results

Effect of adding CO_2. CO_2 from a commercial supply cylinder was passed into the steel cylinder L where the pressure was measured by means of the gauge M. From this cylinder the CO_2 passed through a metal tube which was kept at a temperature such that the CO_2 was at room temperature when it entered the chamber J at K. A buffer plate was placed across the tube so as to insure a more complete mixing of the CO_2 with the air.

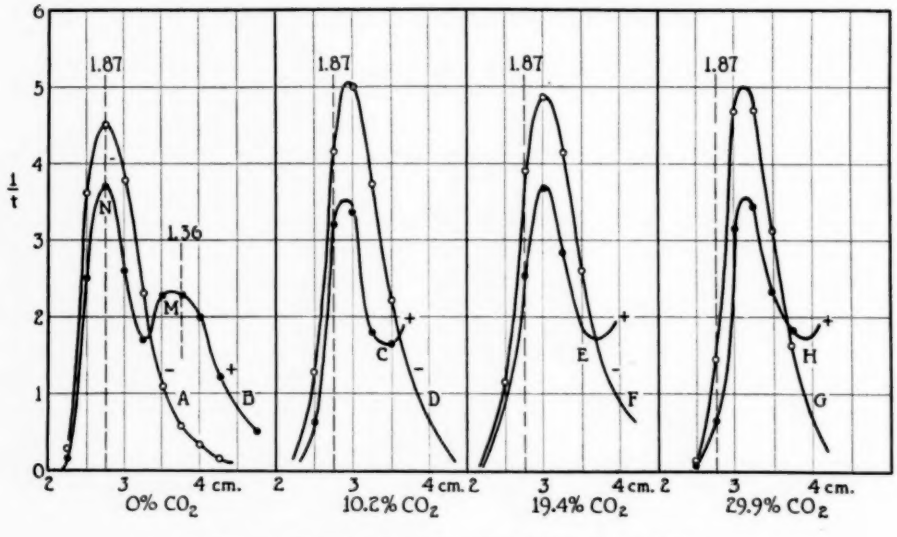

Fig. 2. Showing how CO_2 diminishes the mobility.

The ions were produced, by means of the alpha-rays from polonium, in the air passing through the tube T from the room. The rate of flow of the air between the plates A and B was determined with an anemometer. The rate of flow of the CO_2 at the pressures indicated by the gauge M was determined with a gasometer. The percentage of CO_2 was computed from these two rates.

The results obtained are shown graphically in Fig. 2. Curves A and B were obtained when only air passed through the tank J. Curve A is for the negative ion and as usual has only a single maximum which appears at a down-stream distance of 2.75 cm, and corresponds to a mobility of 1.87

cm/sec per volt/cm. Curve *B* is for the positive ions and has a maximum *N* due to the initial positive air ion at 2.75 cm, the same as for the negative ion, and a maximum *M* at 3.75 cm which corresponds to a mobility of 1.36 cm/sec per volt/cm, and is due to the final positive air ion. The age of the ions in this case was such that a portion of the initial positive ions had transformed into final ions as indicated at *M*. Curves *C* and *D* show the position of initial positive and negative maxima when 10.2 percent of CO_2 is added to the air in the mixing tank. The vertical dotted line shows the positions of the maxima in the case of air only. Curves *E* and *F* are for a 19.4 percent mixture and curves *G* and *H* for a 29.9 percent mixture. It is thus seen that a decided lowering of the mobility takes place as more CO_2 is added. In Fig. 3 is shown graphically the variation of the mobility with percent of CO_2 added.

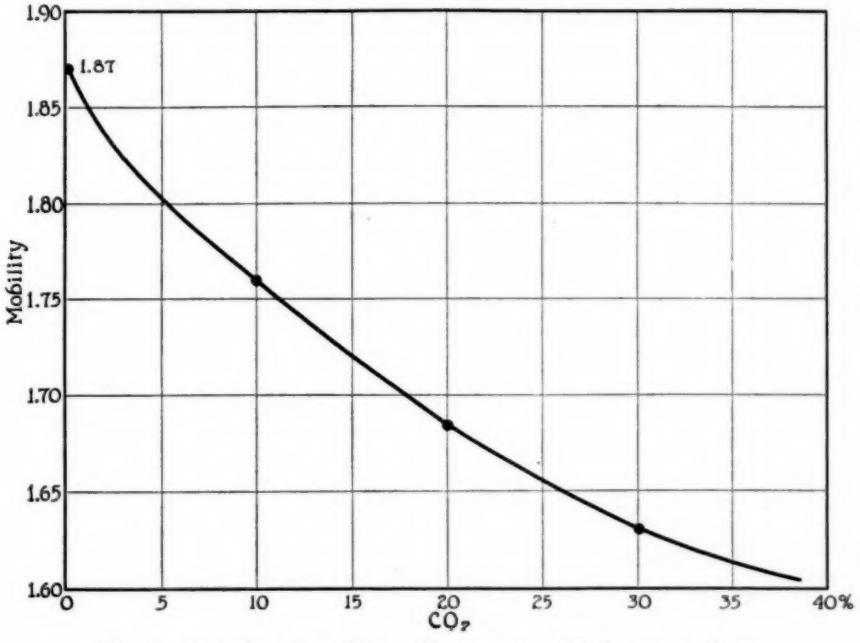

Fig. 3. Variation of mobility with percent of CO_2 in the medium.

It is of interest to know if the observed change in the mobility is in this case due to a change in the ions or to the change of the medium only or both. Evidence bearing on this question is offered by the character of the shifts observed. In Fig. 4 curves *A* and *B* are for air only. Curve *A* shows one negative ion and curve *B* shows the initial positive ion and the final positive ion and the proportion of each. Curves *C* and *D* are the corresponding curves in the case of air plus CO_2. It is seen that the curves *C* and *D* are similar to the curves *A* and *B*, not only in width but also in the relative amounts of the initial and final positive ions. This could not possibly be the case if there were a change in the nature of the ions. If the ion changed in going from *E* to *F*, Fig. 1, the curve would broaden out instead of shifting as a

unit, as is observed. Furthermore, if a change in the ions takes place it is quite inconceivable that the relative amounts of the two positive ions would remain unaltered. It seems therefore that the conclusion must be that the ions remain unaltered and that the change in the mobility is due, in this case, only to the altered medium which interposes a greater resistance to the motion of the ions. This increase in the resistance to motion is probably due to an increase in the specific inductive capacity of the medium. The charge of the ion exerts a greater polarizing action on the surrounding medium when CO_2 is added to the air.

Effect of adding hydrogen to the medium. The procedure in this case was similar to that in the case of carbon dioxide. The hydrogen from a commercial supply cylinder was admitted to the cylinder *L*, Fig. 1. It was then allowed to discharge through *K* under a pressure of 7 cm. This gave a mixture of about 12 percent of hydrogen.

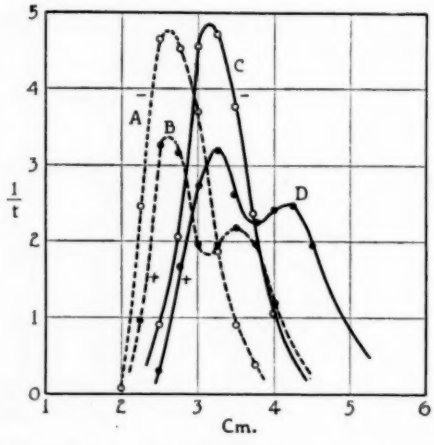

Fig. 4. Showing that the mobilities of all ions present are changed by the same amount.

The results obtained are given in Fig. 5. Curves *A* and *B*, Set (a), are for air only and curves *C* and *D* are for the 12 percent hydrogen-air mixture. It is thus seen that the presence of hydrogen increases the mobility by about 20 percent. It is also seen that the mobilities of both the initial and final positive ions are increased by the same percent and that the increase of the mobility of the initial positive ions is the same as the increase in the case of the negative ion. It is also seen that the proportion of initial and final positive ions is not appreciably altered. In this case therefore as in the case of CO_2, the change is due to the medium and not to a change in the ion.

The greater height of the curves for the hydrogen-air mixture (Curve *CD*) is due to the greater slope of the ionic stream. In order to test this point the downstream distance of the electrode *F*, Fig. 1, was kept constant and the potential between the plates *A* and *B* varied. Curves (b), Fig. 5, show the results. Curves *E* and *F* are for air only and curves *G* and *H* are for the 12 percent hydrogen-air mixture. It is seen that there is no significant alteration in the altitude of the curves.

Effect of adding water vapor to the medium. Tyndall and Grindley[1] observed the effect of moisture on the mobility in air and found that the mobility diminished as moisture was added. In their case the air and the moisture were in a closed vessel as the alternating field method was used. The changed medium in which the mobility was measured was thus also the medium in which the ions were produced by the rays.

It is of interest in this case to know if the change observed was due to the change in the medium through which the ions moved or if it was due to a change in the ions. The same apparatus described above could be used for this purpose. The most satisfactory method for introducing the moisture was to increase the relative humidity of the air in the room. In order not to change the air in which the ions were produced the tube T, Fig. 1, was

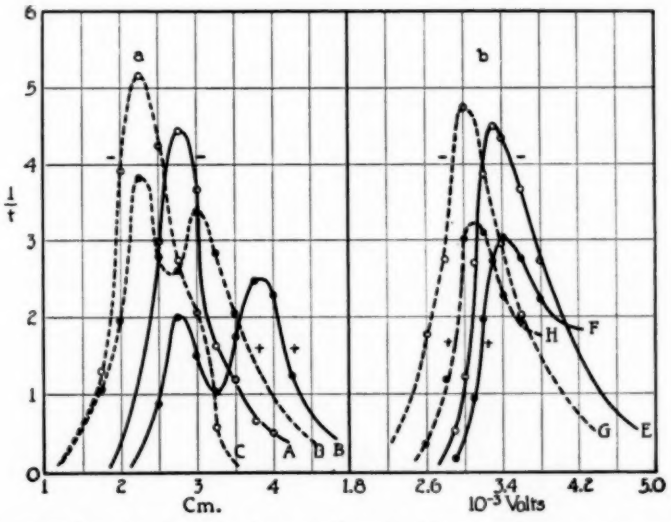

Fig. 5. Showing the effect on the mobility of adding hydrogen to the medium.

connected to a three-inch pipe which passed into the adjoining room. The unchanged ion from T thus passed into the moist medium at E, thus permitting a separation of the effect of the moisture in the medium from the ionizing process. As an alteration in the temperature of the medium at constant pressure produces a detectable effect, it was necessary to keep the temperature of the room constant. The procedure therefore was to raise the temperature of the room to 29°C and obtain a set of curves with normally dry air. The humidity in the room was then raised by evaporating water keeping the temperature constant at 29°. A set of curves under the new condition was then obtained.

The results are shown in Fig. 6. Curves A and B, Set (a), are for a relative humidity of 25 percent and C and D are for a relative humidity of 65 percent. Curve E is for the negative ion when the humidity was again 27 percent and shows the return to the normal mobility value.

[1] Tyndall and Grindley, Proc. Roy. Soc. **A110,** 358 (1926).

The curves in set (b), Fig. 6, were obtained under conditions similar to those for set (a). Here however the voltage between plates *A* and *B* was changed instead of changing the downstream distance of *F*, Fig. 1. The full curves *F* and *G* are for normally dry air and curves *H* and *I* are for air of 65 percent humidity. It is thus seen that the effect of water vapor is to diminish the mobility as found by Tyndall and Grindley.[1] The question of interest is: To what extent is this change in the mobility due to a change in the ions.

The sharpness and similarity of the negative curves indicate that there has been no change in the negative ion and that the change in the mobility of the negative ion is due to the change in the medium. The presence of water vapor in the medium increases the resistance to the motion of the negative ion. In the case of the initial and final positive ions there is also a corresponding decrease in the mobility. The presence of water vapor in the medium thus retards the motion of the initial and final positive ions by the same amount as it retards the negative ion.

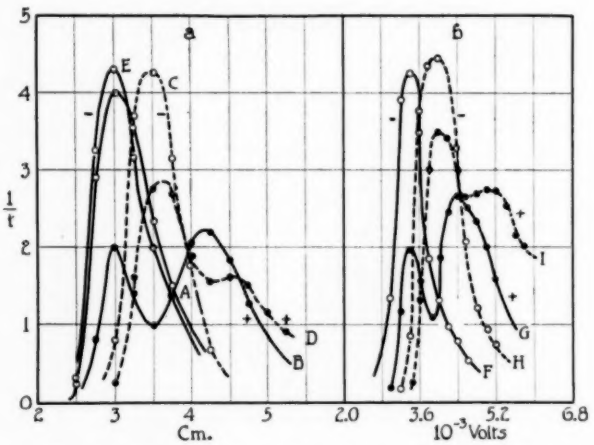

Fig. 6. Showing effect of water vapor on mobility.

An interesting effect here comes into evidence when it is noted that the relative number of initial and final positive ions is altered by a change in the humidity, and, strangely, that the number of initial ions is greater at the higher humidity. This has the apparent effect of slowing up the transition of the initial positive ion into the final ion, an effect observed by Tyndall and Grindley.[1] Mrs. Valasek[2] met with it in her work on the time of transition of the initial into the final air ion. The writer has also met with it on a number of occasions and has been greatly puzzled by it. The effect is as if the final positive ion in the presence of water vapor simplifies back to the initial ion state.

The writer has felt for some time that the effect was due to a more ready attachment to a water cluster on the part of the final ion. The heavy ion thus formed being carried downstream out of reach of the measurement

[2] Leila M. Valasek, Phys. Rev. **29**, p. 542 (April, 1927).

and thus giving an apparent increase in the ratio of the initial to the final ion. The fact, however, that the height of the maximum for the initial ion increases with the humidity rather precludes this interpretation as this indicates that there is an actual increase in the number of initial ions. If it is the final positive ion which is simplified by the water the effect would have to take place when the ion entered the moist air at E, Fig. 1, and would thus have to be of a rapid order. That such rapid changes may take place at E is borne out by the results for acetylene to be described presently. In the case of water vapor it is as though its presence loosened the electrical bond between the two molecules of the final positive air ion.

Effect of adding acetylene to the medium. In the case of acetylene it had previously been found[3] that the initial and final positive air ions disappeared and that a positive acetylene ion was formed which is distinctive in that it has a slightly lower mobility in air than the negative air ion and therefore may be recognized. It was therefore decided to add acetylene to the air in J, Fig. 1, and observe to what extent a transfer at E is detectable. The results obtained are shown in Fig. 7.

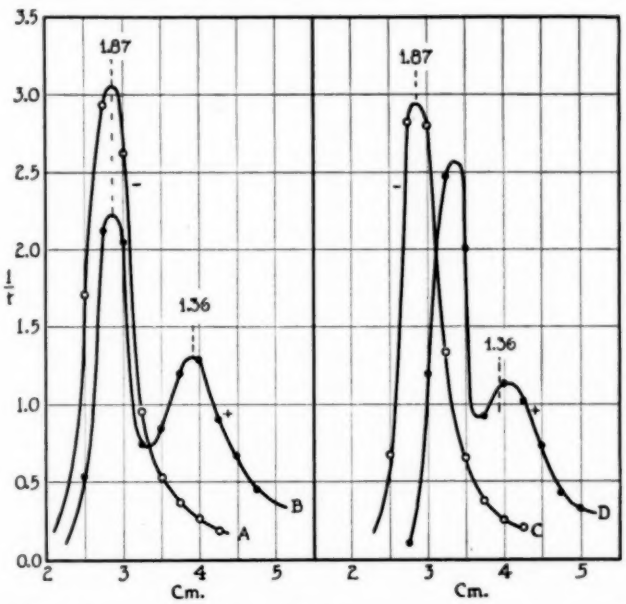

Fig. 7. Showing effect on mobility of adding 0.01 percent acetylene to the medium.

Curves A and B were obtained using air without the acetylene and curves C and D when acetylene was mixed with the air in tank J. It is thus seen that while the negative is not changed in position, the first maximum of the positive has shifted to the normal position of the positive acetylene ion as found in the investigation on acetylene.[3] It is also seen that the initial positive ions have changed completely and that the final ion has also changed, but by a smaller amount. That the position of the final 1.36 ion has not

[3] Erikson, Phys. Rev. **28**, p. 372 (August, 1926).

changed, however, is significant. The writer feels that what takes place here is that the acetylene molecule gives up an electron to an air ion forming a positive acetylene ion. This ion behaves as if it has a slightly greater polarizing action and thus meets with a slightly greater resistance to motion.

The above shows that the effect of the acetylene at E is sufficiently rapid to permit of its detection. The amount of acetylene added was of the order 0.01 percent indicating the great sensitiveness of the effect. This amount was too small to alter the medium sufficiently to change the mobility as in the case of CO_2.

Anomalous effect in the case of acetylene. In working with acetylene it was found that the results were not the same, if the acetylene gas were admitted to the air at K, the far end of tank J, Fig. 1, as the results obtained when the acetylene was admitted at N, a point near the inlet to the apparatus. The results are shown in Fig. 8. Curves A and B are for air without the acetylene.

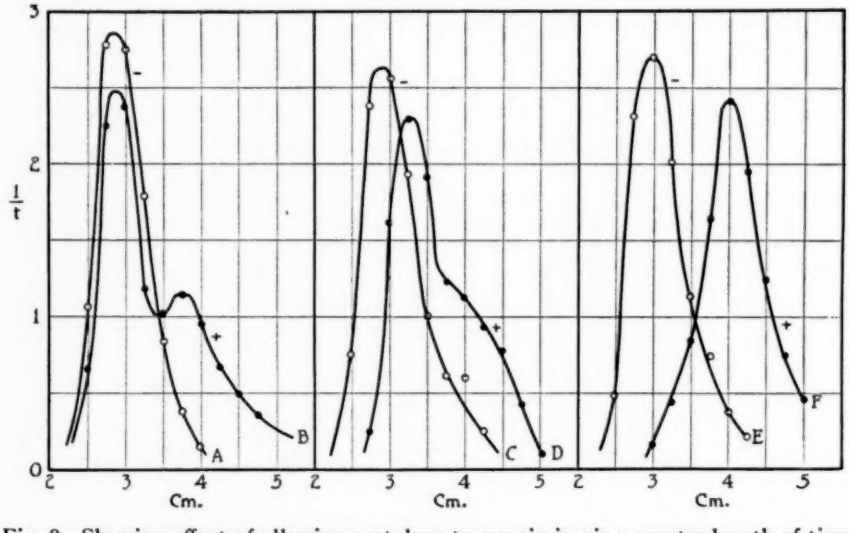

Fig. 8. Showing effect of allowing acetylene to remain in air a greater length of time.

Curves C and D were obtained when acetylene was admitted at N about 15 cm from inlet to tube AB. Curves E and F were obtained when the acetylene was admitted at K, the remote end. It is thus seen that a gradual change takes place when acetylene remains in the air. When acetylene is first admitted to the air the acetylene molecules are free and will give up an electron to the positive air ions thus forming a one molecule positive acetylene ion which, as shown by curves CD, Fig. 8, and as was found in the earlier investigation,[3] appears to have a mobility a little less than 1.87, the mobility of the negative and initial positive air ions. It is seen from curves E and F, Fig. 8, that acetylene unites with the air forming a body which upon becoming charged through contact with the positive air ions at E, Fig. 1, manifests itself as a 1.36 or two-molecule ion.

Effect of adding ethylene, chlorine, and ammonia to the air. In these cases a glass tube 4 meters long and 6 cm inside diameter was substituted in place

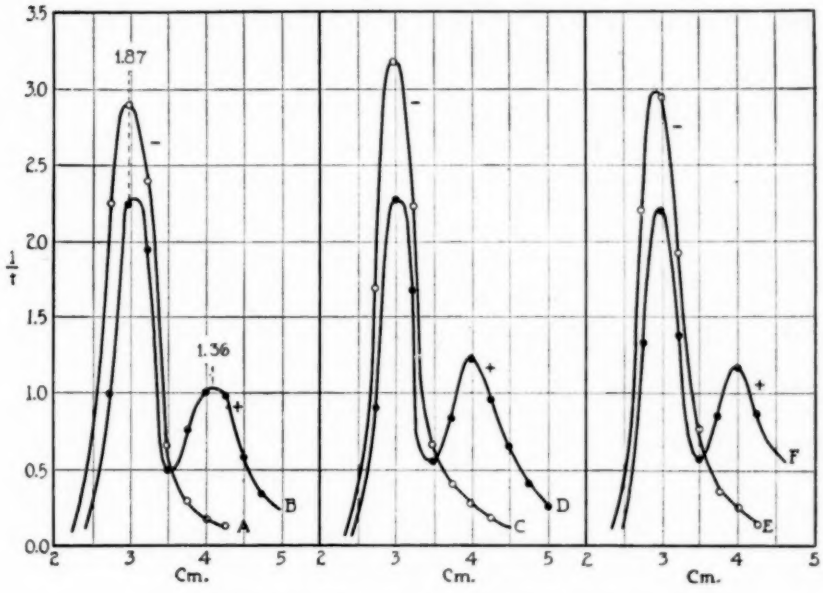

Fig. 9. Showing no effect in adding ethylene to the medium.

of the metal tank *J*, Fig. 1. The gases were admitted at the near end and at the remote end of this tube. The results in the case of ethylene are shown in Fig. 9. Curves *A* and *B* are for air only. Curves *C* and *D* were obtained when the ethylene gas was admitted at the near end, and *E*, *F*, when admitted at the far end. The amount of ethylene added was the same as in the case of acetylene. It is seen that no effect is obtained.

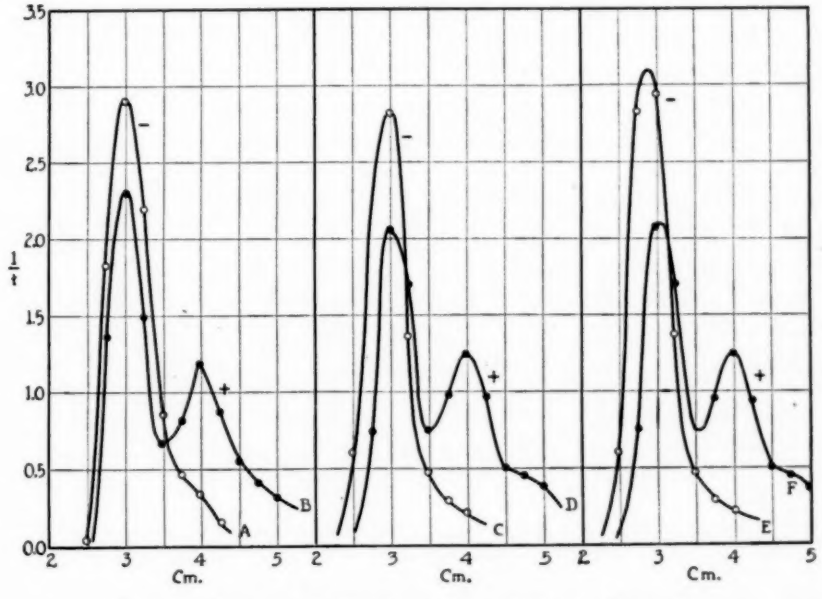

Fig. 10. Showing no effect in adding chlorine to the medium.

In Fig. 10 are given the curves obtained when chlorine is added. *A* and *B* are for air only, *C* and *D*, with the chlorine admitted at the near end, and *E* and *F* at the remote end. Here again there is no change unless the slight increase in the negative is significant.

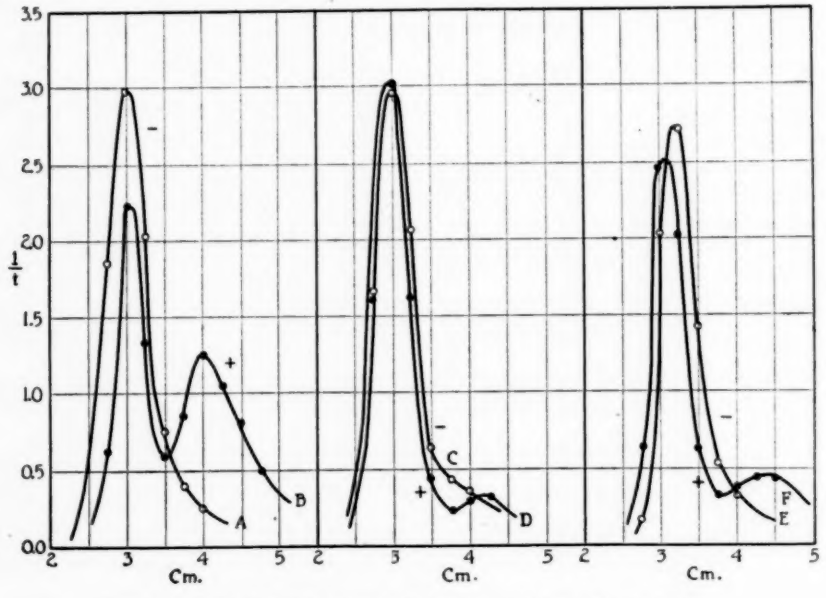

Fig. 11. Showing effect of adding ammonia to the medium.

In Fig. 11 are given the results of adding ammonia to the air. Curves *A* and *B* are for air only, *C* and *D* for ammonia admitted at the near end, and *E* and *F* at the remote end. Here a decided effect is obtained similar to the effect with acetylene.[3] The final positive air ion has disappeared and a single positive ion of the same mobility as the negative air ion is obtained. This has the effect as in the case of acetylene of increasing the positive ion mobility. This effect of ammonia was first observed by Loeb.[4] This effect is as if the ammonia simplifies the final positive air ion or that an ammonia molecule gives up an electron to the positive air ions and thus itself becomes a one molecule positive ion.

It is to be observed that the mobility of the negative ion is slightly decreased when the ammonia has been in the air from the remote end indicating that a slight change has taken place.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA.
June 11, 1927.

[4] Loeb, Nat. Acad. of Sci. **12**, p. 677 (Dec., 1926).

A MECHANICAL MAXWELL DEMON

By J. L. Costa, H. D. Smyth and K. T. Compton

Abstract

A direct experimental verification of Maxwell's distribution law.—A beam of molecules was directed through radial slits in two disks mounted about 8 cm apart on a common shaft which rotated at a speed from 500 to 6000 rpm. in a highly evacuated enclosure. Those molecules which, because of a favorable relation between their velocity and the speed of rotation of the disks, passed through the slits, fell on the vane of a sensitive radiometer. The variation of the radiometer deflection with the speed of the disks was observed for hydrogen, nitrogen and carbon tetrachloride. The form of the curves varied with the nature of the gas and was in agreement with the predictions of the kinetic theory, thus constituting a rather direct confirmation of Maxwell's distribution law. It is feared, however, that it is not possible at present to develop the apparatus sufficiently to obtain a "velocity spectrum" of the neutral molecules in a gas as was the original hope of the writers.

IT IS a curious consequence of the electrical nature of matter that we can study atoms and molecules more easily when they are ionized than when they are in the normal electrically neutral state. If we are dealing with ions we can control their paths and speed, measure the ratio of their charges to their masses and in general study their behavior as individual particles but when dealing with normal molecules we still have to depend on statistical effects such as pressure, density, and temperature. In many phenomena, however, particularly in gaseous chemical reactions, it would be of great interest if we could determine the exact nature of the uncharged particles present just as we can determine the nature of the charged particles present in a discharge tube by the use of positive ray analysis. An attempt to achieve this end experimentally is described in the present paper. Though it was not sufficiently successful to be used as a method of "neutral ray analysis" it did give an experimental verification of Maxwell's distribution law which is thought to be of interest.

According to the kinetic theory of gases the average kinetic energy of all the molecules in a gas at a given temperature is the same and therefore if some of the molecules are of smaller mass than others they must have greater velocity. Moreover, the velocities of molecules at ordinary temperatures are always of the order of several hundred meters per second, a magnitude not far from realizable mechanical speeds. Long ago Maxwell suggested that molecules of differing velocities might be separated by the intervention of his infinitesimal but highly intelligent "demons." It occurred to the writers that vacuum technique had progressed to the point where a mechanical Maxwell demon might be possible.[1]

[1] Stern (Zeits. f. Physik **2,** p. 49, 1920) had already made a direct measurement of the molecular velocities in the case of a metallic vapor and Tykocinski-Tykociner (Jour. Op. Soc. Am. **14,** p. 423, May 1927) has recently published a plan for an experiment similar to the one described here.

The principle of the experiment may be best understood by reference to the schematic diagram in Fig. 1. Suppose a stream of gas is emerging from the slit S_1 into a highly evacuated space. Some of the molecules will have such velocities that they will pass through the radial slits s_1, s_2 · · · in the periphery of the rotating disk D_1; in particular, a few will continue through the second rotating disk, through the second fixed slit S_2 and impinge on the mechanical detecting system R, a radiometer. The molecules of this group, however, will no longer be of all velocities. Since their time of passage from D_1 to D_2 must be such that they will find a slit in D_2 in front of S_2, the beam will consist of molecules of one or more definite ranges of velocity depending on the dimensions of the apparatus and the speed of rotation of the disks.

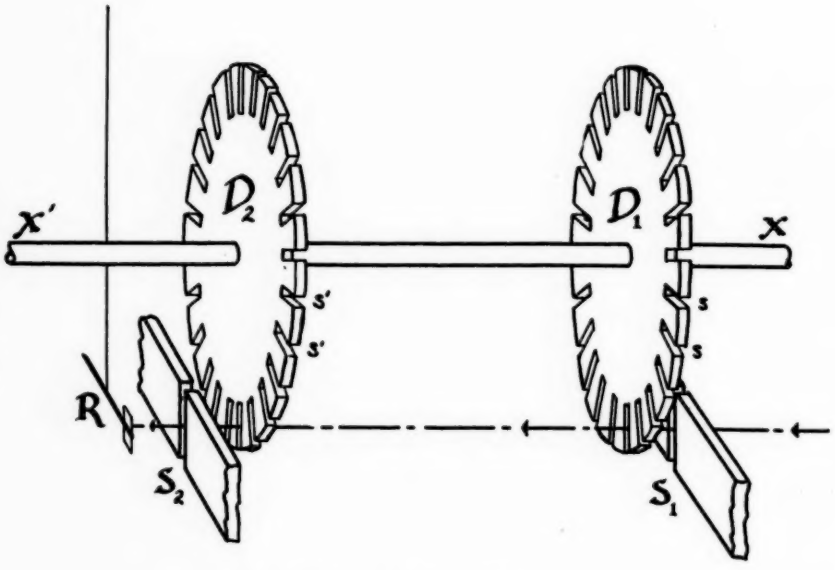

Fig. 1. Schematic diagram of apparatus.

Consider a simple case. Suppose the gas emerging from S_1 consists of two kinds of molecules of differing mass but in temperature equilibrium. Then there will be molecules of two velocity groups corresponding to the Maxwell distribution around the mean velocities for the two kinds of molecules. Let the number of molecules passing through S_2 be studied as a function of the speed of rotation of the disks. If there is only one slit in each disk a maximum should occur corresponding to the movement of the slit in D_2 in front of S_2 in the time of passage of each type of molecule from D_1 to D_2. The total number of molecules passing through S_2, however, will be very small and difficult to detect. On the other hand if there were a large number of slits in D_2 then at such a speed that the fast molecules get through the first slit s_1' coming in front of S_2, the slow molecules get through the second or third and the maxima are obscured. However, since this effect is calculable and

the chief difficulty to be feared is that of insufficient intensity the latter case seems to offer a better chance of success.

Apparatus and Procedure

The drawing in Fig. 2 represents the apparatus as realized. Inside the cylindrical bronze casting B are set two flanges F_1 and F_2 in each of which is a sapphire bearing accurately aligned along the axis of the cylinder. These bearings carry the shaft A on which are mounted two duralumin disks with radial slits cut in their peripheries. Also on the shaft A is the rotor R of the electromagnetic driving system. It is actuated by the stator M. The glass window W_1 gives a view of the rotor from outside, thus allowing the

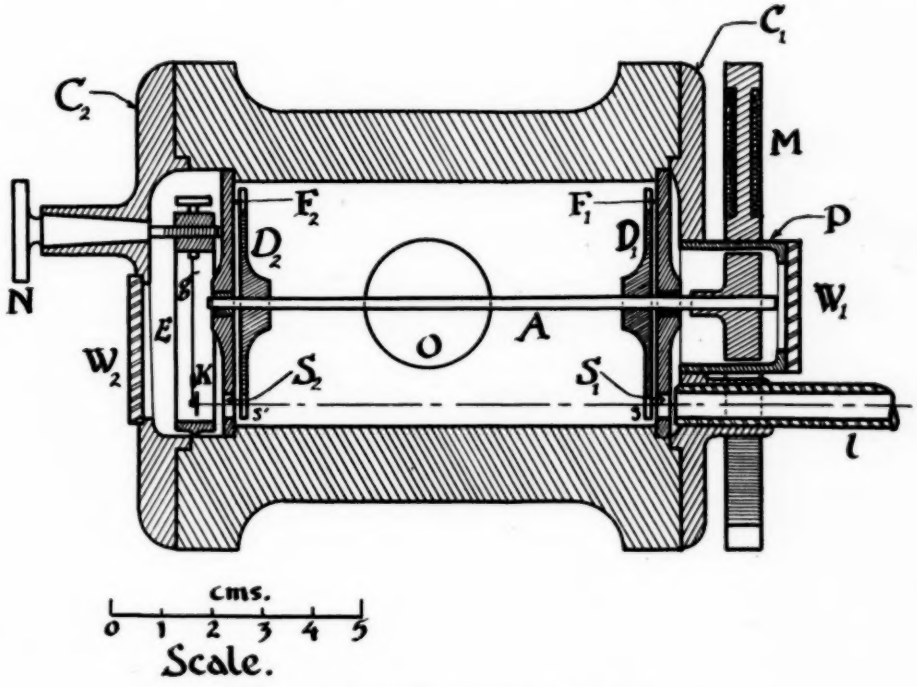

Fig. 2. Diagram of apparatus as realized.

speed to be measured. Gas is fed in through the glass tube l to the slit S_1 and evacuation is through O by big tubing to a rapid diffusion pump. E is the radiometer mount with suspension z and the delicate movable system k. This system carried a small mirror which was illuminated through the window W_2. A radiometer, rather than some other detector of the molecular beam, was chosen principally because of its insensitivity to the action of stray molecules not included in the primary beam coming through the slits. The movable system weighed between one and two mg, was supported by a delicate quartz fiber, was rendered conducting by sputtering in order to eliminate electrostatic disturbances, and was given a slight magnetic control in virtue of unavoidable magnetic properties. The whole apparatus was

constructed with a view to solidity and freedom from vibration and was bolted down to a concrete pillar.

Varying the speed of the rotary converter which supplied the current to M made it possible to vary the speed of R between 500 and 6000 r.p.m.

The procedure in an actual experiment was to observe the deflection of the radiometer as a function of the converter speeds, the latter then being reduced to speeds of rotation of the slit system by a stroboscopic calibration. Small deflections due to secondary causes and varying with the speed of the rotating system were measured and allowed for in the experiments.

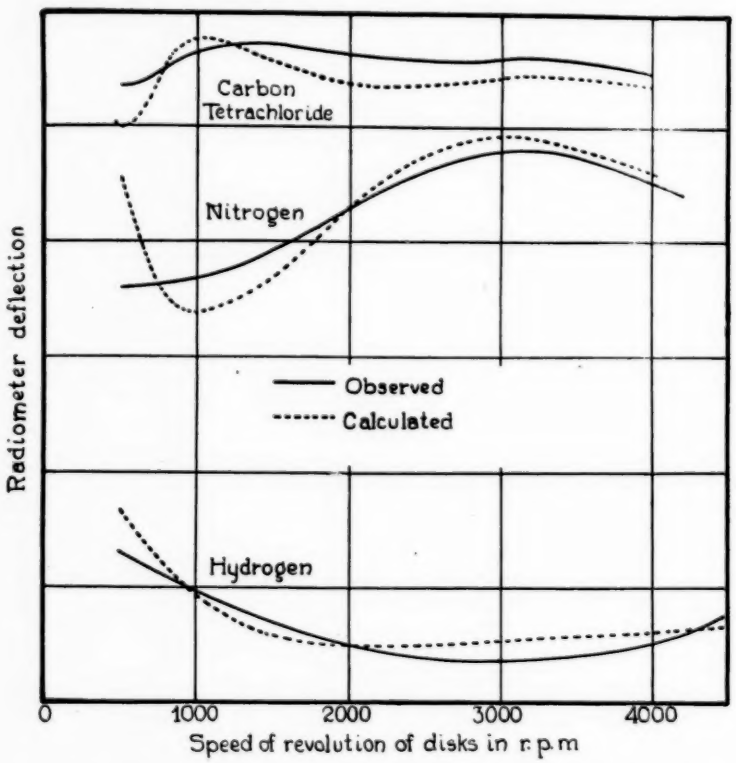

Fig. 3. Variation with speed of the disks of the radiometer deflections.

Results

It was found that when a pure gas was used quite consistent and reproducible results were obtained and that the form of the curves varied with the nature of the gas. This may be seen from Fig. 3 where the experimental curves are averages of several runs. At first sight the comparative flatness of the maxima was disappointing but a theoretical analysis of the situation showed that the curves predicted by kinetic theory were actually in good agreement with the observations.

The calculations involved are a little tedious but quite straightforward and need not be reproduced here. First the probability of a molecule getting

through to the radiometer is calculated as a function of the speed of the molecule. As it will depend on the speed of rotation of the disks as well as the distribution of the slits in the periphery and the other dimensions of the apparatus, we need to calculate curves for various speeds of revolution. Then for every molecular speed we multiply this geometrical probability by the kinetic theory probability of a molecule having that speed and by the speed itself. This gives numbers proportional to the numbers of molecules of various speeds passing through to the radiometer. Again this calculation must be repeated for various speeds of rotation of the disks. Up to this point the only assumption made is that the molecules have a Maxwellian distribution of velocity.

In order to find the torque produced in the radiometer by the impact of these molecules on its vane it is necessary to make an additional assumption. Two possibilities suggest themselves. First that the molecules are not reflected or are reflected with a velocity proportional to their velocity of impact. This means that they contribute to the vane an amount of momentum proportional to their velocity and we obtain a number proportional to the total torque on the radiometer at a given speed, by multiplying the number having a given velocity by that velocity and integrating over all values of the velocity. It was by this procedure that the theoretical curves in Fig. 3 were obtained.

The second possibility is that the molecules are reflected with Maxwell distribution of velocity characteristic of the temperature of the vane. This would mean a contribution to the torque proportional to the number of molecules striking in addition to the part of the torque proportional to the product of the number striking and their velocity. This more complicated case has not been worked out in detail but has been considered sufficiently to conclude that it would simply cause a slight flattening of the maxima in the theoretical curves obtained in case 1.

In considering the agreement between the experimental and theoretical curves in Fig. 3 several points should be mentioned. At the low speeds, the difficulty of controlling the speed accurately is greater and the theoretical large torque would also be obscured by the simultaneous increase in stray effects. At all speeds there is an unknown amount of periodic deviation of the induction motor from exact synchronism ("creeping") which would tend to blur the maxima. Finally the radiometer had to be used at nearly the limit of its sensitivity which made the observations difficult.

It is thought therefore that the agreement is as good as could be expected and constitutes a rather direct confirmation of Maxwell's distribution law although not distinguishing between the two mechanisms of reflection suggested above. It is feared, however, that it is not possible at present to develop the apparatus sufficiently to obtain a "velocity spectrum" of the neutral molecules in a gas as was the original hope of the writers.

WOONSOCKET, R. I. (J. L. C.)
PRINCETON, N. J. (H. D. S. and K. T. C.)
June 25, 1927.

NOTE ON THE BARKHAUSEN EFFECT UNDER MECHANICAL STRESS

By E. P. T. Tyndall and J. M. B. Kellogg

Abstract

Voltage pulses are induced in a solenoid surrounding a strip of magnetic material under mechanical stress. These pulses occur in both directions, giving direct proof of atomic orientation in a particular direction, but in either sense. Possible hypotheses for the smallness of the effect in comparison with the magnetic Barkhausen effect are advanced.

McKeehan[1] has recently pointed out that there is an orientation in a particular direction of the atomic axes in a magnetic material which is in a state of tensile stress. The orientations of the individual axes, however, do not agree in sense, since tension alone would then produce magnetization. The occurrence of such an orienting effect is inferred from parallel changes of resistance caused either by tension or by a magnetic field. That changes in orientation occur discontinuously seems to be shown by the existence of a mechanical[2] Barkhausen effect, which, as far as can be judged by the sound produced in the phones in the method of observation usually used, is identical with the ordinary (magnetic) Barkhausen effect. There should, however, be a fundamental difference. Discontinuities in magnetization produce uni-directional voltage impulses[3] in a surrounding solenoid due to changes in orientation of atomic axes, the final orientations at magnetic saturation being in one sense only. The effect of tension or other mechanical stress should produce similar voltage impulses but these should occur in *both* directions. It seemed worth while to the writers to make a direct test of this point in the fashion described below.

The output of a four-stage, resistance-coupled amplifier is connected across two deflector plates of a cathode ray oscillograph[4] while a suitable 60 cycle voltage, placed across the other two deflector plates, sweeps the spot back and forth at right angles to the deflection produced by the amplified voltage. The sensitivity of the oscillograph is about 7 volts per cm deflection. The first three stages of the amplifier contain *CX*-340 tubes and the fourth a *CX*-301*A* tube. Coupling resistances are 250,000 ohms and blocking condensers 0.1μF. The voltage amplification at 60 cycles, measured by means of the oscillograph, is 35,000. To the input is connected a 10,000 turn

[1] McKeehan, Jour. Frank. Inst. **202**, p. 737 (1926).

[2] Zschiesche, Zeits. f. Physik. **11**, p. 201 (1922), also gives previous references. Gerlach, Zeits. f. Physik. **39**, p. 327 (1926).

[3] Tyndall, Phys. Rev. **24**, p. 439 (1924).

[4] J. B. Johnson, Jour. Op. Soc. Am. and R.S.I. **6**, p. 701 (1922).

solenoid, 2.5 cm long, which surrounds the specimen of magnetic material. One end of the latter is clamped rigidly, while the other is fastened to a brass rod passing through brass collars, so that by twisting or pulling this rod by hand, the specimen is subjected to the corresponding stress.

The results obtained are in entire accord with what was expected. The effect is shown in a very marked manner by a strip of silicon steel $5 \times 0.3 \times 0.05$ cm. While it is being twisted through 10 or 15 degrees, deflections of more than 2.0 cm occur. These are in both directions apparently equal in magnitude and number, though the method of visual observation is not well suited to forming an accurate judgment of the number of impulses. While the specimen is being pulled or is being released exactly similar deflections occur but on the average only about half as large. When this same specimen is magnetized by bringing a strong magnet near it, deflections are produced (uni-directional, as noted above) which exceed the extent of the screen and the amplifier is obviously overloaded.

As the individual voltages generated by the mechanical effect are so small compared to those generated during magnetization one is led to believe that, if in both cases the same volume of material acts as a unit in which simultaneous reorientation in the same sense occurs, then the degree of rearrangement is much less for the mechanical than for the magnetic effect. If, on the other hand, each impulse corresponds to magnetic saturation of a small volume, then the volume acting as a unit must be much less in the mechanical case. There is of course a third possibility if a small volume is not thought of as acting as a unit. The observable magnetic effect would then consist in the random coincidence of elementary events (rearrangement of single atoms) agreeing in sense but too small for individual record, while in the mechanical effect the coincidence would occur between elementary events differing in sign. Thus the algebraic sum of these events would be less, even for events of the same magnitude and with the same number occurring per unit of time.

It may also be stated that when the specimen is placed in a magnetic field, produced by an adjacent horseshoe magnet, the mechanical effect is apparently less. In this case, moreover, while small deflections in both directions may be observed for a very slight twist, a larger twist produces mostly uni-directional impulses due to actual changes in the magnetization of the specimen, which is in a constant field but under varying mechanical stress. These deflections are in one direction for either direction of twist with increasing torque, and in a reverse direction when the specimen is released, the magnetic field being in the same direction throughout.

A soft iron wire, 1.3 mm in diameter, shows effects similar to those observed for silicon steel for both torsion and tension, though only about one-fourth as great. The two cases are not, however, really comparable in view of the great difference in the magnitude and distribution of stresses in the two specimens whose shapes are dissimilar. Also in the specimen of

circular cross section the individual events would have a longer duration, due to the increased time constant[5] of the induced eddy currents, and there would, therefore, be a greater degree of overlapping of effects of opposite sense which occur close together in time. Nickel wire, whether annealed or drawn, shows no effect of this character under mechanical stress.

PHYSICAL LABORATORY,
UNIVERSITY OF IOWA,
June, 1927.

[5] Tyndall, loc. cit., p. 450.

BOOK REVIEWS

Equilibria in Saturated Salt Solutions. W. C. BLASDALE. In this book the author discusses the equilibria obtained in heterogeneous systems of from one to six components of which water is always one component, the others being derived from acids, bases or salts. The book is not an exhaustive compilation of experimental data but is rather an attempt to exhibit the most useful methods of studying and describing the properties of heterogeneous systems. This object is achieved by the discussion of a series of typical systems for which fairly complete data are available. Chemists will undoubtedly find this volume of great value. Although van't Hoff, Roozeboom, Schreinemakers and many other chemists are referred to, it is astounding to find no mention in this book of a certain Yale professor who is generally supposed to have laid the foundations for the thermodynamic treatment of heterogeneous systems. Pp. 197, 78 figs. The Chemical Catalog Co. New York. 1927. $4.50.

F. H. MACDOUGALL

Die Grundlagen der Wärmeübertragung. FRIEDRICH MERKEL. This is the fourth volume of the technical series "Wärmelehre und Wärmewirtschaft" and is an exposition—in some cases quite extensive—of the types of heat transfer of technical importance. After a brief chapter on conduction in a solid the author takes up at once the main subject, the transfer of heat between a solid and a fluid with either forced or free convection. The theory is developed mainly on a hydrodynamical basis with frequent numerical illustrations. Curves and formulas are given for the solution of such problems as the temperature attained by a fluid passing down a length of pipe, the velocity of the fluid, diameter of pipe and temperature of its walls being given. The treatment is carried out for a large variety of cases, including bent tubes, bundles of pipes and even flat walls. The practical importance—as well as the difficulty—of such problems will be recognized at once. Succeeding chapters take up radiation and some minor matters.

The references are largely to engineering periodicals. One is a little surprised at the omission of the names of certain physicists, e.g., Smoluchowski; but in all fairness it should be stated that the author does not take up the transfer of heat from a gas to a solid by pure conduction, which is one of the cases in which, as a branch of kinetic theory, physicists have been largely interested. On the whole the book may be considered a welcome contribution to the literature of the subject. Pp. 234+xi, 88 diagrams. Theodor Steinkopff, Dresden and Leipzig. 1927. 15 R.M.

L. R. INGERSOLL

Die elektrische Leitfähigheit der Atmosphäre und ihre Ursache.—VICTOR F. HESS. After a brief historical introduction the electrical conductivity of the atmosphere is the subject of the next chapter. It includes the theory of ionization of gases, methods of measuring the electrical conductivity of air and the determination of the number of ions present with results of such determinations; a discussion of the methods of measuring ionic mobilities; and measurements of mobility and the number of large ions (Langevin ions). The third chapter deals with the causes of ionization. The ionizing agents are discussed under headings (1) agents of non-radioactive origin, (2) radioactive substances, solid and gaseous, found in the atmosphere and (3) the penetrating radiation of which the author was one of the first investigators and which is frequently named after him in the German literature: the Hess'sche Strahlung. The fourth chapter deals with the loss of ions by adsorption, diffusion and recombination. The final chapter contains a comprehensive discussion of the cause of the residual ions (1) in the atmosphere near and above land, (2) above sea, (3) in the troposphere, i.e. at heights to abuot 9 km, and (4) in the layers of the atmosphere 11 km and more above the surface of the earth. Experiments and theory dealing with the Kennelly-Heaviside layer are discussed in some detail.

The monograph is concluded with a bibliography of German books dealing with atmospheric electricity and with a name index and a subject index. Throughout the book one is impressed with the attempt to bring the material up to date and in this attempt the author was successful. Pp. 174+viii, 14 figs. Sammlung Vieweg. Heft 84–85. Friedr. Vieweg and Sohn Akt. Ges., Braunschweig. 1927.

ALOIS F. KOVARIK

Probleme der γ-Strahlung. FRITZ KOHLRAUSCH. The author is well-known for his investigation of γ-rays especially in the field of absorption and scattering. In the introduction to this memoir he gives reasons for using the title "Problems of the γ-rays" in preference to "Physics of the γ-rays" which are obvious, namely, that the field is by no means settled but still presents various difficulties. The work is scholarly and thorough in the presentation of known experimental facts and their theoretical explanations which are critically discussed. There are ten sub-divisions including a general survey of the field, γ-rays and the electromagnetic theory presented from Sommerfeld's and from J. J. Thomson's points of view, photoelectric and Compton effects, counting single γ-ray entities, description of the methods of determining the wave-lengths of γ-rays, namely, from photo-electric determinations, from absorption coefficients, and from interference data giving the results obtained by these methods, and absorption and scattering. The author concludes with a comprehensive review of the problems, with explanation of the formulae used in the discussions and a complete bibliography and index. Pp. 155+viii, 27 figs. Sammlung Vieweg. Heft 87–88. Friedr. Vieweg and Sohn Akt. Ges., Braunschweig. 1927.

ALOIS F. KOVARIK

Radioaktivität. ST. MEYER and E. SCHWEIDLER. Second edition. The first edition of this excellent work was received not only as a thorough treatise on the subject of radioactivity but also as a source of a very complete bibliography on the subject up to the year of publication, 1916. The present edition meets these requirements up to 1927. During the intervening decade more than 1500 researches in various parts of radioactivity have been published. Some of these have only added new or more accurate data while others have solved some of the existing problems as, for example, the relation between the β-rays and the γ-rays, and others have, furthermore, brought in new subject matter and new problems, as, for example, the investigations of isotopes and of atomic disintegration. As a result of this, the new edition is rewritten in many places and new subject matter is added. Material from allied fields has been included only in so far as it has strictly any bearing on radioactivity. The first edition contained 541 pages and 87 figures while the present edition contains 721 pages and 108 figures. Besides the necessary changes in the text, there are in the addendum tables of constants for the α-rays, β-ray spectra, and the γ-ray wave-lengths as obtained by the various methods. From the references to the Bull. Nat. Res. Council No. 51 it is clear that this bulletin on radioactivity which reviewed critically the literature between the time of Meyer and Schweidler's first edition and June 30, 1924, is given due recognition. Pp. 721+x, 108 figs. B. G. Teubner, Berlin. Bound 36 R.M.

ALOIS F. KOVARIK

Aus Leben und Beruf—Aufsätze. Reden. Vorträge. FRITZ HABER. A collection of thirteen addresses and lectures delivered in Germany and abroad during the period 1921 to 1927 upon the subjects: Eightieth Birthday of Carl Engler (1922); German Chemistry in the Last Ten Years (1923); Address at the Celebration of the Fiftieth Anniversary of the Akademisch-Literarischen Vereins in Breslau (1924); Science and Life (1924); Japanese Impressions (1924); Address to the Japanese Minister of Education upon Presentation of a Collection of German Books in the Ministry of Education (1924); Scientific Relations between Germany and Japan (1925); Cultivation of Science (1925); Status of the Question of the Transmutability of the Elements (1926); The Boundaries of Chemistry (1926); Address at the Opening of the Japan Institute (1926); State and Science (1927); Appendix: Die Notgemeinschaft der deutschen Wissenschaft (1921).

These addresses have a broad appeal to those interested in the economic and scientific post-war problems with particular reference to chemistry and Germany's effort to establish a close scientific and economic alliance with Japan.

Professor Haber's assertion that the various efforts to effect transmutation of the elements have hitherto been unsuccessful is especially significant in view of his experimental tests of some of the recent claims. Pp. 173+vi, 1 fig. Julius Springer, Berlin, 1927. 5.70 R.M. bound.

S. C. LIND

Das elektromagnetische Feld. EMIL COHN. This is a text-book of Electricity and Magnetism. It is divided into the following parts: Electrostatics; magnetostatics; quasistationary fields; propagation of the field; newer developments. The latter include the theory of electrons and of moving bodies following Lorentz, and restricted relativity.

No emphasis is laid on detailed physical theories such as Langevin's theory of magnetism, or Debye's dipole theory. Neither does the author pay much attention to variational equations and Lagrangian functions. The treatment is almost entirely given from the point of view of Maxwell's equations. Solutions of electrostatic problems are presented. However, they are not systematized as in Jeans. General principles are frequently illustrated by examples from engineering practice. As a text-book the book has a distinct advantage in not being too voluminous and containing the most essential parts of the subject. Pp. 366, 41 figs. Julius Springer, Berlin, 1927. 24 R.M.

G. BREIT

The Internal Constitution of the Stars. A. S. EDDINGTON. In the first chapter of his important book the author surveys the problem of the structure, upkeep, and development of the individual star. The remainder of the book contains the detailed working out of the opening theme, beginning with expositions of the relevant quantum theory and thermodynamics, and proceeding to the analytical discussion of polytropic gas spheres and the theory of radiative equilibrium. The principles developed for the purpose are then applied to the analysis of the intimate detail of stellar conditions. The composition and ionization of the stellar interior, the relation between mass and luminosity, the source of stellar energy, and the theory of stellar variation are discussed at length, the balance between matter and energy that results in the existence, maintenance, and fluctuation of stars appearing as various aspects of cosmic physics.

The last two chapters, which deal with "The Outside of a Star" and with "Diffuse Matter in Space" do not strictly fall within the province of the book. The former describes the physics of the stellar atmosphere, and the latter involves the problem of the nebulae and of interstellar clouds—subjects that are still in a highly tentative stage. The last chapter, in fact, avowedly carries less finality than the remainder of the book, and will doubtless provoke some opposition.

"The Internal Constitution of the Stars" will of course become standard equipment for every astronomer. To the physicist it will appeal not as a treatment of terrestrial physics applied to astronomy, but of cosmic physics, often (as in the discussion of the absorption coefficient, and the source of stellar energy) emphasizing broader aspects of the subject than can be touched in the laboratory. The book is hardly for the general reader, but it is written with the familiar lucidity that does not shrink from expressing in plain language ideas that can so be expressed. Only the mathematical physicist is competent to appraise the technical parts of the book. But its greatest use will be to the astronomer and the astrophysicist, because it makes available to them the ablest modern conclusions in the theory of their subject, never avoiding the issue nor obscuring doubtful points, and always proceeding with great clarity. There are times when the sufficiency and representativeness of the data used are open to question, as with the material used for the mass luminosity curve. In fact, one of the values of the book is that it will indicate to the practical astronomer the data that are in most need of improvement. The importance of Professor Eddington's latest contribution to the literature of astronomy cannot be overemphasized. Pp. 407+viii. Cambridge University Press, 1926.

CECELIA H. PAYNE

Handbuch der Physikalischen Optik. Edited by E. GEHRCKE, Volume 1. Second Half.—The mathematical theory of optics takes up the larger part of this half of the first volume. This makes the book a valuable addition to optical literature and fills a need that has existed for several years. The contents include, briefly, interference (concluded from the first half); diffraction; theory of light; phenomena at boundaries between two media such as reflection, refraction, total reflection and the accompanying polarization effects; dispersion and absorption; double refraction; polarization; optical activity; and ponderomotive effects of light. Since the particular phenomena treated in this volume are most effectively bound together by the electromagnetic theory of light and the classical electron theory of matter, the few scattered quantum developments are either omitted or receive bare mention. However, there is included a good discussion of the quantum theory interpretation of the constants which appear in the dispersion formula. A few of the newer developments included in this volume are the lattice theory and diffraction of Röntgen rays, the mathematical theory of diffraction, Debye's theory of molecular refraction, and Born's theory of optical activity. However, in more ways than these, it is a work of great merit. Pp. 471+x, 139 figs. Verlag von Johann Ambrosius Barth, Leipzig, 1927. 32 R.M. unbound.

JOSEPH VALASEK

Données Numériques de Spectroscopie. L. BRÜNINGHAUS. Extract from Vol. V of "Tables Annelles de Constantes et données numériques de Chimie, de Physique, et de Technologie." This book of tables is a collection of all the important numerical data of spectroscopy published in the years 1917 to 1922 inclusive. It was perhaps not intended that any particular editorial supervision should be exercised over the material, but that the responsibility should be left entirely with the authors, however divergent the results. As space did not permit the inclusion of absolutely everything that appeared in these years, the personal equation of the editor did however enter in a decided manner. Roughly speaking, half the articles mentioned are referred to by title only, and opinions will differ as to which pieces of work should have been so treated. One notes, for instance, that Paschen's important articles on the structure of the spectrum of neon are among those listed by title only; the remarkable discovery by Paschen and Back (1921) of the effect of a magnetic field in causing the emission of "forbidden" lines is not even mentioned; in fact no articles appearing in "Physica" are quoted; and yet space is found for plenty of minute details of other sorts.

The date of publication of this work is three years after the last articles reproduced in it. Unfortunately, the rate of growth of spectroscopy is so rapid that the book was out-of-date before it was published. In the light of present day knowledge, the emphasis seems often to be misplaced.

The arrangment of the book is somewhat confusing. Band spectra are everywhere classed with line spectra. While there is a separate sub-chapter entitled "Emission of X-rays" (including a reference to J x-rays) one runs into x-ray data in another chapter on fine-structure, sharing a page with details of helium bands. On a following page are found the L doublet of neon, classified as an item in fine-structure, side by side with certain echelon—ghost fine-structures which deserve a quiet burial. A later page contains oxygen absorption bands, lead and "Ra C" (meaning Ra G) x-rays and scandium multiplets. Finally, x-ray absorption edges occur still later on, mixed with absorption curves of inorganic solutions. "Series of lines and bands" share a very large chapter together, in spite of their very fundamental difference. In this chapter there is room for brief accounts of two articles by the same author on the same subject with the same results, printed one after the other. King's temperature classification of the lines of Fe, Mn and Sc one might look for in chapter V "Influence of conditions of excitation on the characteristics of line spectra," sub-heading 1 "Influence of Temperature;" but it is really found under chapter IV, "Influence of temperature or pressure on the constitution of emission spectra." The page headings do not help in finding subjects, one heading, in four languages, recurring unchanged for 265 pages. The table of contents is concealed amongst conspicuous advertising matter of other books, and the chapter headings are so modest as to be almost unrecognizable. Fortunately, a helpful index enables one to find what he is looking for, if he knows in advance what that is.

The part of the book that will probably be most useful is that dealing with the absorption spectra of solutions, organic liquids, etc., in which field there are few convenient recent summaries. Pp. 350. Gauthier-Villars, Paris, 1925.

F. A. SAUNDERS

Tabelle der Hauptlinien der Linienspektra aller Elemente nach Wellenlänge geordnet. H. KAYSER. This little volume is much more than a revision of the similar set of tables given by Professor Kayser at the end of the sixth volume of his Handbuch der Spektroskopie. It is a completely new and up-to-date list of the stronger lines of all the elements, arranged in order of wave-lengths from far in the ultra-red (9μ) to the last wisp of a line (124 A. U.) in the extreme ultra-violet. For the first time we find here only International wave-lengths, the Rowland scale being officially and finally abandoned. The newer measurements are so good that the third decimal place frequently appears, and the author's keen critical sense has been advantageously applied to all measurements, so that one may have confidence in the wave-lengths as far as they are carried out. Where many values are available, a weighted mean is given, and no one could better be trusted with this delicate task than Professor Kayser. The new list contains nearly twice as many lines as the old one, and takes in, quite rightly, many of the fainter lines in the more difficult regions of the spectrum. One welcomes especially the appearance in this book of designations such as Ca II, Al III, etc., referring to the spectra of more or less ionized atoms. While perhaps not more than a tenth of the lines given are thus labelled as coming from the complete atom, or from the chemically and spectroscopically different atoms obtained by removing one electron or more, the rapid increase in our knowledge of this part of spectroscopy will enable us to add information of this sort as it appears, and the author has arranged wide margins and good paper, so that such notes may be put into the book itself.

There seem to be remarkably few misprints. The reviewer notes the inclusion of the secondary spectrum of hydrogen among line spectra, though before the date of the preface (March 1926) there was no doubt that this spectrum was due to the molecule; and no other band spectra seem to be given. Also we find another survival of the days when the same atom was thought to have two or more spectra, in the retention of the terms "red" and "blue" spectrum of argon. It would be more in harmony with current practice to call the red spectrum A I, while the blue spectrum is doubtless a mixture of A II, A III, etc., depending on the violence of the excitation. A few late papers missed inclusion in the list; we note the absence, for instance, of Lyman's He II series beginning with $\lambda 303$ published in 1924, and his main series in He I ($\lambda 584$, etc.) published in 1922.

It is ungracious, however, as well as difficult, to find flaws in this excellent piece of work. All active spectroscopic workers will unite in thanking Professor Kayser for the indomitable spirit and admirable persistence which he has shown in continuing his long series of labors in spite of serious difficulties, and in producing this indispensable volume. Pp. 198. Julius Springer, Berlin, 1926. 24 R.M.

F. A. SAUNDERS

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE RENO MEETING, JUNE 23, 1927.

The 146th regular meeting of the American Physical Society was held in Reno, Nevada, at the Mackay School of Mines, in affiliation with the Pacific Division of the American Association for the Advancement of Science. The meeting of that Association included general research reports, Wednesday, June 22, and other meetings and excursions extending through Saturday, June 25. The meeting of the American Physical Society was held Thurdsay, June 23, the morning session beginning at 10 o'clock. The afternoon session was a joint session with the Astronomical Society of the Pacific. The program consisted of seventeen papers of which abstracts are given in the following pages. An **Author Index** will be found at the end.

D. L. WEBSTER
Local Secretary for the Pacific Coast

ABSTRACTS

1. A translucent black "board." W. WENIGER AND H. R. VINYARD, Oregon Agricultural College.—The solution of a difficult problem in blackboard illumination was obtained by abandoning the usual opaque board and substituting therefore a ground glass surface uniformly illuminated from the rear. With the customary room illumination, part daylight and part electric, everything on this "black board" was visible from all parts of the room, even from points making an angle of only 10° with the plane of the writing surface. Incidental advantages gained are: ease of erasure; ability to use the surface as a translucent screen for projecting lantern slides with the possibility of adding chalk lines to projected diagrams; ability to intersperse chalk talks with lantern slides without changing the general room illumination.

2. Remarkable electrical conditions accompanying west Texas sand storms. E. F. GEORGE, W. M. YOUNG AND HARRY HILL, Texas Technological College.—During West Texas sand storms the atmosphere is in a very unusual electrical condition. Severe shocks are sometimes received from radio antennas, fence wires and automobiles. Automobile ignition systems refuse to function in very severe storms. A radio antenna composed of stranded wire 0.19 cm in diameter and 33.75 meters long stretched at an elevation of 72.7 feet in an east and west direction between towers 282 feet apart, formed the basis of preliminary measurements. Prevailing storms are from the west. Potentials of over 40,000 volts, as measured by spark gap between spherical electrodes, have been obtained. Direct currents as high as 1.2×10^{-4} amperes have been measured. This corresponds to an atmospheric current density of 1.88×10^{-7} amperes per square centimeter, provided voltage and current are unaffected by friction of sand against wire. This value of atmospheric current density is about 10^{8} times as great as that given in Humphrey's "*Physics of the Air*." Further measurements will be made with vertical wire to test the effect of direction and velocity of wind and quantity of sand carried.

3. Gas ion mobilities in $C_2H_2-H_2$ mixtures. L. B. LOEB AND L. DU SAULT, University of California at Berkeley.—The effect of NH_3, which forms an NH_4^+ ion in solution, in markedly

raising the mobility of positive ions in H_2 gas, and the fact that C_2H_2 forms complex metal ions in solution which, according to Erikson, give mobilities of positive and negative ions that are almost equal, led the writers to study ion mobilities in $C_2H_2-H_2$ mixtures. The values found for mobilities in pure C_2H_2 which have not been carefully determined before were 0.708 cm/sec per volt/cm for the positive and 0.769 cm/sec per volt/cm for the negative ions on the generally accepted standard of 1.8 cm/sec per volt/cm for negative ions in air. On the new Absolute Standard of Loeb and Tyndall and Grindley, in which the negative ion in air has the mobility of 2.15 cm/sec per volt/cm, these values are 0.846 cm/sec per volt/cm for the positive ion and 0.906 cm/sec per volt/cm for the negative ion. It was found that the mobility of the negative ion was higher than that of the positive, because of the fact that the negative ion, even at atmospheric pressure, spends part of its career as a free electron. The mobilities in $C_2H_2-H_2$ mixtures could be computed within the limits of error from the theoretical equation, thus indicating the absence of any marked clustering on either ion and that the phenomenon occuring in NH_3-H_2 mixtures does not occur in $C_2H_2-H_2$ mixtures. These results indicate that positive and negative ions in C_2H_2 have the same mobility and that no specific clustering occurs. They thus explain observations of Erikson which appeared to introduce serious difficulties in Erikson's theory of ionic nature and the ageing effect, so that as regards C_2H_2 no serious contradiction to this theory is now encountered.

4. Internal pressures of pure liquids and liquid mixtures. W. WESTWATER, H. W. FRANTZ AND J. H. HILDEBRAND, University of California at Berkeley.—The senior author has shown that ideal solutions can only be formed from liquids having identical values of the coefficient $(\partial P/\partial T)_V$, which is designated γ. Internal pressure may be defined as γT. Experimental determination of values of γ has been made for 8 pure liquids and for 13 of their 50 mol percent mixtures, in order to secure data of importance in studying the deviations of solutions from ideality. The relation between P and T is linear over a range of 20 atmospheres, the slope depending upon the mol volume of the liquid. The following values were obtained in atmospheres per degree for the mol volume corresponding to 20° and 1 atmosphere. (1) heptane, 8.91; (2) carbon tetrachloride, 11.72; (3) carbon disulfide, 12.95; (4) benzene, 12.92; (5) ethylene chloride, 14.67; (6) bromoform, 16.08; (7) acetone, 11.66; (8) ethylene bromide, 15.87. The 50 mol percent mixtures of the foregoing, referred to by numbers, are as follows: 1–6, 11.03; 2–4, 12.37; 3–4, 12.53; 4–5, 13.18; 4–6, 14.40; 1–7, 9.59; 1–2, 9.89; 1–3, 10.02; 1–4, 10.04; 1–8, 10.97; 3–7, 12.10; 3–8, 14.33; 6–8, 15.94. The values for the mixtures are less than additive and the departure is greater than that calculated from an equation of Biron $\gamma_1\gamma_2/(\gamma_1 N_1+\gamma_2 N_2)$, where N_1 and N_2 represent mol fractions of the constituents.

5. Intermittent photographic exposure as affected by wave-length and intermittency ratio. CLARENCE E. WEINLAND, Stanford University. (Introduced by George R. Harrison). The intermittency effect has been investigated at various wave-lengths in the visible and ultraviolet as far down as λ2537. Intermittent exposures produced by any one of a number of sector discs, each giving a different ratio of flash to rest, allowed any of the following variables to be changed without affecting any other: wave-length, light intensity, frequency of flash, and ratio of flash to rest. The time of exposure was constant at 14 seconds. Cramer Contrast Process and Wratten Panchromatic plates showed a decrease in density of from 15% to 25% with intermittent exposure, this decrease under certain conditions being at λ4358 double its value at λ2537. Eastman 33 and Speedway plates showed only a small intermittency effect, independent of wave-length. On the first two emulsions the difference between densities from intermittent and continuous exposures increased with the ratio of rest period to flash period. An exponential relation fitted this data, at any one set of conditions the difference between densities increasing as a power of the intermittency ratio. It was shown that very large photometric errors can arise when spectra of a spark source are measured on plates calibrated with a non-intermittent source.

6. Band spectra and dissociation of iodine monochloride. G. E. GIBSON AND H. C. RAMSPERGER, University of California at Berkeley.—Thirty-three band heads of ICl were measured in absorption and found to consist of two series, one of them converging at 17410 ± 30 cm^{-1}

($\lambda = 5744$A). Two heads of a third series were faintly in evidence just beyond the convergence, fading out in the region of continuous absorption. The maximum of continuous absorption is about 4800A. Intensity variations with temperature indicate that all three series come from excited states of normal ICl, the observed convergence coming from the first vibrational level. The vibration frequency of normal ICl is 380 cm^{-1}. Interpreted according to the theory of Franck our results indicate that ICl dissociates in light (1) into unexcited atoms, (2) into an unexcited iodine atom and a chlorine atom in the 2^2P_1 state. The convergence corresponding to dissociation into chlorine and excited iodine was not found. Combined with the optical data of Kuhn on Cl_2 and I_2 our results require an evolution of 3.8 Cal. for the reaction $ICl = \frac{1}{2}I_2 + \frac{1}{2}Cl_2$, assuming the observed convergence to correspond to process (1). Thermodynamic data give 3.5 Cal. for the same reaction. The two faint heads of the third series probably correspond to (2). The thermodynamic measurements are susceptible of accuracy sufficient to exclude definitely other possible interpretations.

7. An electron-quantum theory of galvanomagnetism and thermomagnetism. A. E. CASWELL, University of Oregon.—As yet no satisfactory theory has been proposed to account for the positive sign of the Hall effect and similar discrepancies between observed data and the simple electron theory of this and allied phenomena. The author offers an explanation of the four transverse galvanomagnetic and thermomagnetic effects based upon (1) the well-known behavior of electrons in a magnetic field, (2) an increase in the concentration of free electrons in a metal with rise in temperature, (3) the emission of quanta within a solid conductor, (4) the collision of quanta with electrons according to the laws of mechanics, as applied in the explanation of the Compton effect, and (5) the deflection of a quantum within a metallic conductor by a magnetic field in the same direction as an electron and according to a similar law of force. The first four items are scarcely open to argument. The fifth is a new hypothesis for which the justification rests upon its usefulness in the explanation of observed facts. The theory may be extended to explain the longitudinal effects and gives promise of being valuable in the theory of metallic conduction.

8. Effect of a magnetic field upon thermal conductivity of iron, copper, silver and gold. HUGH M. BROWN, University of California at Berkeley.—In this work the thermal conductivity is measured in both longitudinal and transverse fields by O' Day's application of the "Bar Method." The bars were 4" long, and $\frac{1}{8}$" in diameter. The precision was sufficient to easily detect a change in thermal conductivity of 0.1 percent. Longitudinal fields of 10,000 and 5,000 gauss, and transverse fields of 8,000 and 4,000 gauss were used. In iron, the longitudinal field produced a decrease of 1.14 percent in the heat conductivity. The transverse field of 4,000 gauss decreased the heat conductivity of 0.4 percent, while in the field of 8,000 gauss, the change was less than 0.1 percent. This behavior parallels the change in resistance of iron observed by others. For copper, the two longitudinal fields decreased the thermal conductivity 0.23 and 0.21 percent respectively. The transverse fields produced no change as great as 0.1 percent. In silver and gold, none of the fields produced as much as 0.1 percent change. The resistance of iron was increased 0.2 percent by the longitudinal field of 10,000 gauss, while no change in resistance was observed in the other metals. No change could be detected in the thermal e.m.f. constant of the thermocouples. Thus, copper, the only non-magnetic metal showing an appreciable effect, behaves as the magnetic ones, nickel and iron. Livens' theory predicts an increase in the thermal conductivity by the magnetic field, and hence is not checked by this research.

9. Magnetic spectrum of secondary electrons. J. B. BRINSMADE, California Institute of Technology.—An aluminum target was bombarded with homogeneous streams of primary electrons (velocities ranging up to 172 volts) and the velocity distribution of the resulting secondary electrons studied with a magnetic analyser and electrometer. Other observers report a peak near the primary velocity and a broad distribution with a low velocity hump. The present apparatus has sufficient resolving power to show that the former peak is extremely sharp consisting only of electrons "reflected" from the target with no appreciable loss of energy. The coefficient of reflection is of the order of 10^{-3} per unit solid angle at the deviation used

(approximity 90°). It increases somewhat with decreasing primary velocity. At this deviation, the full velocity electrons constitute about 2% of the secondary current with 172 volt primary velocity and 10% with 34 volt.

10. An experimental study of the relative intensities of x-ray lines in the L-spectrum of thorium. SAMUEL K. ALLISON, University of California at Berkeley.—The relative intensities of the thorium L-series lines at 31.8 kilovolts have been measured using an ionization spectrometer with methyl iodide in the ionization chamber. The relative intensities of the lines at high voltage was calculated from the observed intensities at 31.8 kilovolts by studying the variation of the intensity of the lines with voltage. It was found that this could be expressed in the range studied by $I=k(V-V_0)^2$. The results are corrected for absorption inside and outside the ionization chamber. The intensity rules for the doublets hold for the lines involving L_{21} and L_{22}. The predictions of Wentzel based on Schrödinger's mechanics for the relative intensities of "sharp" and "diffuse" doublets are confirmed, but the experimental intensities of the "principal" series doublets are too low by a factor of 7. They are also too low in the measurements of Jönsson on tungsten.

Line	l	α_2	α_1	η	β_6	β_2	β_7	$\beta_1+\beta_5$	β_3	γ_5	γ_1	γ_2	$\gamma_3+\gamma_6$	γ_4
Obs. Int.														
31.8 kv	3.6	12	100	1.1	1.4	26	.45	38	1.8	0	8.5	.81	3.1	0
Calc. Int.														
High voltage	3.6	12	100	1.8	1.4	26	.45	62	3.3	0	14	1.5	5.3	0

11. Direct and indirect ejection of K electrons by cathode rays. DAVID L. WEBSTER, Stanford University.—When cathode rays strike a block of metal, they may eject electrons from the K orbits of atoms, either by direct action or by an indirect, photoelectric process, through continuous-spectrum x-rays. The present experiments distinguish these two types of K ionizations by their mean depths in the metal, the indirect being deeper. Two methods were used. One was by determination of the ratio of $K\alpha$-line intensity of silver to continuous-spectrum intensity of the same wave length (ratio of line area to continuous-spectrum ordinate) for rays emerging from the surface at 20°, 5° and less than 1°. The other method was by calculation from relative intensities of $K\alpha$ lines from a composite target, made of a block of cadmium covered with silver, thick enough to stop cathode rays but thin enough to let through a reasonable fraction of the x-rays. The first method showed merely that a majority of the K rays were from direct ionizations. The second, with three different thicknesses of silver, showed that at 50 kv (nearly 2 V_K) the ratio of direct ionizations to indirect was 2.4, with a mean deviation 7%, and probable error somewhat greater.

12. Large losses of energy by cathode rays: ratio of the probabilities of the two types. DAVID L. WEBSTER, Stanford University.—Cathode rays penetrating a heavy element may lose energy in large amounts, either by imparting it to atomic electrons or by radiating quanta belonging to the continuous spectrum. Let Q be the ratio of the probability that a cathode ray ejects a K electron to the probability that it radiates a continuous spectrum quantum with $\nu>\nu_K$; and let P be the ratio given in a previous abstract in this program, of the probability of K ionization by direct action of a cathode ray to K ionization by indirect, photoelectric action. Then if the energy distribution in the continuous spectrum is known except for a constant factor, the ratio Q can be calculated, from it and P. Using Kulenkampff's continuous-spectrum formula, it appears that for silver at 50 kv., Q is nearly unity. Some change in Q with voltage may occur in silver; and a comparison with Beatty's and Unnewehr's data indicates that Q for copper is two or three times as great. Incidentally, in silver at 50 kv, the indirect Kα-line rays carry energy equivalent to a region of continuous spectrum about 30′ wide, and the direct rays about 70′.

13. The theoretical relation between infra-red and ultra-violet bands. R. T. BIRGE AND J. J. HOPFIELD, University of California at Berkeley. According to the present interpretation of band spectra, the frequency of infra-red (vibration-rotation) bands of a diatomic molecule can be calculated from the measured frequencies of certain ultra-violet (electronic) bands

correlated with the normal state of the molecule. Carbon monoxide furnishes the only quantitative test known thus far. Schaefer and Thomas observed infra-red bands at 4.67μ, 2.35μ, and 1.573μ (in air), while Birge (Phys. Rev. **28,** 1168, 1926), from the fourth positive group of carbon, using data of Deslandres and Lyman, *calculated* the infra-red bands as 4.679μ, 2.354μ, and 1.578μ (in vacuum). We have now, from our own plates, obtained more accurate data for this ultra-violet (resonance) system of CO, yielding for the infra-red bands 4.6684μ, 2.3481μ, and 1.5748μ (in vacuum) with a probable error of about one part in 2000, or 4.6672μ, 2.3475μ, and 1.5744μ in air. Because of the greater resolution and sensitivity of the photographic plate, compared to infra-red recording apparatus, the above remarkable confirmation of theory encourages the hope of obtaining infra-red standards from measurements of ultra-violet radiation, in the case of band spectra, as well as in the now familiar case of line spectra.

14. Characteristics of the Neutral and of the singly and doubly ionized spectra of cerium. ARTHUR S. KING, Mount Wilson Observatory. By comparing the arc and spark spectra of cerium with that of the electric furnace, it has been possible to distinguish between the ionized spectrum, which, presumably because of a low ionization potential, forms the major part of the conspicuous lines of the arc, and the spectrum of the neutral atom. The latter, for which the furnace is the only effective source, has been to a large extent unrecognized, at least in the ordinary photographic region. The furnace spectrograms made in the present investigation have permitted the measurement of approximately 1600 neutral lines between λ3000 and λ4700, of which only a few of the strongest had been previously measured in the arc spectrum. In the yellow and red, the neutral spectrum becomes strong in the arc, and has been measured by Kiess and others, so that over 3000 neutral lines may be listed. The very rich spectrum of ionized cerium is common to the arc and spark, while in the ultra-violet a condensed spark discharge gives a large collection of doubly-ionized lines, of which only the strongest group has been previously measured. Preliminary observations indicate that very similar characteristics prevail for the spectrum of the related rare earth, neodymium.

15. The structure of the atmospheric absorption bands of oxygen. G. H. DIEKE, California Institute of Technology, and HAROLD D. BABCOCK, Mount Wilson Observatory. The wave-lengths of all suitable lines were determined by the interferometer. (H. D. Babcock, Astrophysical Journal, **65,** 140, 1927). The others were measured on high dispersion grating plates taken on Mt. Wilson, the broad lines in the A-band by a registering microphotometer. These accurate wave-lengths permit a test of the combination principle, and it is possible to obtain the quantum interpretation of the bands, and confirm the classification of the lines by previous observers. The short wave-length components of the apparent doublets show marked deviations from Deslandres' law in the vicinity of the zero line, whereas no appreciable deviations are found for the long wave-length components. The doublets are electronic doublets and seem really to belong to a triplet system, the other components being forbidden by the selection rules. There are faint doublets which only in the A-band have sufficient intensity to be measured and which have exactly the same structure as the strong ones, the only difference being the value of the constant B(Rotational term $= Bm^2$). The faint and strong doublets have the same zero lines. The moment of inertia of the oxygen molecule in the normal state is 19.27 $\times 10^{-40}$ gm cm.^{2}

16. Pressure effect for iron-arc lines. HAROLD D. BABCOCK. Mount Wilson Observatory. Accurate measurements of the displacement corresponding to one atmosphere change of pressure have been made with the interferometer for about 100 lines in the visible region. Special attention has been given to the elimination of pole-effect from the observations. Members of pressure-groups *a*, *b*, *c*, *d* and *e*, and of 33 multiplets are studied, as well as 17 lines not yet assigned to multiplets. The following summary expresses the present state of the investigation: 1. All wave-lengths increase with pressure. 2. For a given line the change in λ is proportional to the change in pressure. 3. Members of a multiplet behave alike. 4. The pressure displacement is the result of differential depression of the two polyfold terms whose differences correspond to the lines of a multiplet. 5. Assuming the depression of the lowest term in the atom to be zero, the depressions of many higher terms have been derived. 6. For 15

Septet and Quintet terms the decrease in term value is nearly proportional to the square of the level. 7. For Triplet terms a different relation holds. 8. Pressure effect may now be computed for many multiplets not yet measured.

17. Intermittent photographic exposure in various regions of the plate curve.—CLARENCE E. WEINLAND, Stanford University. A previous report has described the effect of wave-length and of ratio of rest period to flash period in intermittent exposure. Further work has given evidence indicating that the incorrect integration of intermittent exposure is intimately associated with the "toe" of the "S" shaped plate curve. At low frequencies of exposure, where each individual flash is as long as one second, the intermittency error is small, and shows no dependence upon the ratio of rest period to flash period. On the other hand, when each individual flash is of less duration than 1/8 second, the error shows a very considerable dependence upon the ratio of rest to flash, and very little upon the frequency of flash. When sufficient continuous exposure is given to result in a density upon the straight line portion of the curve, a subsequent intermittent exposure is integrated properly. A comparison of intermittent and continuous intensity-scale characteristic curves shows that the difference between them increases rapidly with increasing density until the straight line portion of the curve is reached and then remains nearly constant, again indicating that the intermittency failure occurs in the under-exposure region.

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